Diiron and diruthenium aminocarbyne complexes containing pseudohalides: stereochemistry and reactivity

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Abstract

Acetonitrile is easily displaced from $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(MeCN)(Cp)_2][SO_3CF_3]$ (R= 2,6-$Me_2C_6H_3$ (Xyl), **1a**; Me, **1b**) upon stirring in THF at room temperature in the presence of $[NBu_4][SCN]$. The resulting complexes *trans*-$[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NCS)(Cp)_2]$ (R= Xyl, *trans*-**2a**; Me, *trans*-**2b**) are completely isomerised to *cis*-$[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NCS)(Cp)_2]$ (R= Xyl, *cis*-**2a**; Me, *cis*-**2b**) when heated at reflux temperature. Similarly, the complexes *cis*-$[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NCO)(Cp)_2]$ (M = Fe, R= Me, **4a**; M = Ru, R = Xyl, **4b**; M = Ru, R = Me, **4c**) and *cis*-$[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(N_3)(Cp)_2]$ (M = Fe, R= Xyl, **5a**; M = Fe, R = Me, **5b**; M = Ru, R = Xyl, **5c**) can be obtained by heating at reflux temperature a THF solution of $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(MeCN)(Cp)_2][SO_3CF_3]$ (M = Fe, R= Xyl, **1a**; M = Fe, Me, **1b**; M = Ru, R = Xyl, **1c**; M = Ru, R = Me, **1d**) in the presence of NaNCO and NaN_3, respectively. The reactions of **5** with $MeO_2CC{\equiv}CCO_2Me$, $HC{\equiv}CCO_2Me$ and (NC)(H)C=C(H)(CN) afford the triazolato complexes $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{N_3C_2(CO_2Me)_2\}(Cp)_2]$ (M = Fe, R= Xyl, **6a**; M = Fe, R = Me, **6b**; M = Ru, R = Xyl, **6c**), $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{N_3C_2(H)(CO_2Me)\}(Cp)_2]$ (M = Fe, R= Me, **7a**; M = Ru, R = Xyl, **7b**) and $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{N_3C_2(H)(CN)\}(Cp)_2]$, **8**, respectively. The asymmetrically substituted triazolato complexes **7-8** are obtained as mixtures of N(1) and N(2) bonded isomers, whereas **6** exist only in the N(2) form. Methylation of **6-8** results in the formation of the triazole complexes $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{N_3(Me)C_2(CO_2Me)_2\}(Cp)_2][CF_3SO_3]$, **9**, $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{N_3(Me)C_2(H)(CO_2Me)\}(Cp)_2][CF_3SO_3]$ (M = Fe, R = Me, **10a**; M = Ru, R = Xyl, **10b**) and $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{N_3(Me)C_2(H)(CN)\}(Cp)_2][CF_3SO_3]$, **11**. The crystal structures of *trans*-**2b**, **4b·CH_2Cl_2**, **5a**, **6b·0.5CH_2Cl_2** and **8·CH_2Cl_2** have been determined.

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1. Introduction

Pseudohalides are quite versatile ligands, which can coordinate to the metals both terminally or in a bridging fashion [1, 2]. Moreover, when the two end-atoms are different, they can also display linkage isomerism. If the atoms belong to different periods (*e.g* NCS^-, $NCSe^-$), they usually coordinate through nitrogen to 'class a' and *via* sulfur or selenium to 'class b' metals [3]. Conversely, in the case of isocyanates, NCO^-, coordination usually occurs *via* nitrogen, being O-coordination quite rare [3c, 4, 5]. The coordinated pseudohalides behave as 1,3-dipoles and, therefore, can be used in order to prepare new ligands *via* 1,3-dipolar cycloaddition reactions [6, 7].

Herein, we report on the synthesis and reactivity of diiron and diruthenium aminocarbyne complexes containing terminal pseudohalides. This work is part of our ongoing interest in the study of the formation of new C-C and C-N bonds in bimetallic species [8-10], with particular attention to the possibility of selectively addressing the reactions on terminal or bridging ligands and promoting their coupling.

2. Experimental

All reactions were carried out routinely under nitrogen using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Infrared spectra were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. ESI MS spectra were recorded on a Waters Micromass ZQ 4000 with samples dissolved in CH_3CN. All NMR measurements were performed on Varian Gemini 300 and Mercury Plus 400 instruments. The chemical shifts for ^1H and ^{13}C were referenced to internal TMS. The spectra were fully assigned *via* DEPT experiments and ^1H,^{13}C correlation measured using gs-HSQC and gs-HMBC experiments [11]. NOE measurements were recorded using the DPFGSE-NOE sequence [12]. All chemicals were used as received from Aldrich Co., except $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(MeCN)(Cp)_2][SO_3CF_3]$ (R= 2,6-$Me_2C_6H_3$ (Xyl), **1a**; Me, **1b**) and $[Ru_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(MeCN)(Cp)_2][SO_3CF_3]$ (R= Xyl, **1c**; Me, **1d**) [9b] which were prepared by published methods.

*2.1 Synthesis of trans-[Fe_2{μ-CN(Me)(R)}(μ-CO)(CO)(NCS)$(Cp)_2$] (R= Xyl, trans-**2a**; Me, trans-**2b**).*

[NBu_4][SCN] (129 mg, 0.430 mmol) was added to a CH_2Cl_2 (6 ml) solution of [Fe_2{μ-CN(Me)(R)}(μ-CO)(CO)(NCMe)$(Cp)_2$][CF_3SO_3] (0.147 mmol), and the mixture was stirred at room temperature for 3 hours. The solvent was, then, removed under reduced pressure and the residue was chromatographed through alumina. A fraction containing *trans*-[Fe_2{μ-CN(Me)(R)}(μ-CO)(CO)(NCS)$(Cp)_2$] was obtained using CH_2Cl_2 as eluent.

trans-**2a** Yield 52.4 mg (71 %). Anal. Calcd. For $C_{23}H_{22}Fe_2N_2O_2S$: C, 55.01; H, 4.42; N, 5.58. Found: C, 55.32; H, 4.12; N, 5.76. IR (CH_2Cl_2, 293 K): ν(NCS) 2112 (vs); ν(CO) 1968 (vs), 1812 (s); ν(μ-CN) 1549 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 7.42-7.29 (m, 3H, $Me_2C_6H_3$), 4.93 (s, 3H, N*Me*), 4.76, 4.38 (s, 10H, *Cp*), 2.57, 2.41 (s, 6H, $Me_2C_6H_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 345.5 (μ-*C*N), 262.6 (μ-*C*O), 212.5 (*C*O), 148.7 (*C*ipso Xyl), 140.6 (N*C*S), 134.0, 132.4 (*C*-Me Xyl), 129.5, 129.3, 128.5 (*C*H Xyl), 88.9, 87.7 (*Cp*), 53.6 (N*Me*), 18.7, 18.4 ($Me_2C_6H_3$).

trans-**2b** Yield 46.0 mg (76 %). Anal. Calcd. For $C_{16}H_{16}Fe_2N_2O_2S$: C, 46.63; H, 3.91; N, 6.80. Found: C, 46.87; H, 3.72; N, 6.98. IR (CH_2Cl_2, 293 K): ν(NCS) 2115 (vs); ν(CO) 1969 (vs), 1809 (s); ν(μ-CN) 1568 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 4.87, 4.58 (s, 10H, *Cp*), 4.71, 4.31 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 340.6 (μ-*C*N), 263.1 (μ-*C*O), 211.7 (*C*O), 140.8 (N*C*S), 88.9, 87.4 (*Cp*), 52.5, 51.6 (NMe_2).

*2.2 Synthesis of cis-[Fe_2{μ-CN(Me)(R)}(μ-CO)(CO)(NCS)$(Cp)_2$] (R= Xyl, cis-**2a**; Me, cis-**2b**).*

A solution of *trans*-[Fe_2{μ-CN(Me)(R)}(μ-CO)(CO)(NCS)$(Cp)_2$] (0.120 mmol) in THF (10 ml) was heated at reflux temperature for 5 hours. The solvent was, then, removed under reduced pressure and the residue was chromatographed through alumina. The final product *cis*-[Fe_2{μ-CN(Me)(R)}(μ-CO)(CO)(NCS)$(Cp)_2$] was obtained using THF as eluent.

cis-**2a** Yield 56.0 mg (93 %). Anal. Calcd. For $C_{23}H_{22}Fe_2N_2O_2S$: C, 55.01; H, 4.42; N, 5.58. Found: C, 55.32; H, 4.12; N, 5.76. IR (CH_2Cl_2, 293 K): ν(NCS) 2112 (vs); ν(CO) 1989 (vs), 1810 (s); ν(μ-CN) 1507 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 7.42-7.25 (m, 3H, $Me_2C_6H_3$), 4.79, 4.17 (s, 10H, *Cp*), 4.84 (s, 3H, N*Me*), 2.68, 2.27 (s, 6H, $Me_2C_6H_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 341.4 (μ-*C*N), 265.4 (μ-*C*O), 211.5 (*C*O), 148.1 (*C*ipso Xyl), 140.7 (N*C*S), 135.3-128.2 (*C*-Me + *C*H Xyl), 87.3, 86.2 (*Cp*), 53.9 (N*Me*), 18.5, 17.6 ($Me_2C_6H_3$).

cis-**2b** Yield 39.6 mg (80 %). Anal. Calcd. For $C_{16}H_{16}Fe_2N_2O_2S$: C, 46.63; H, 3.91; N, 6.80. Found: C, 46.87; H, 3.72; N, 6.98. IR (CH_2Cl_2, 293 K): ν(NCS) 2112 (vs); ν(CO) 1987 (vs), 1809 (s); ν(μ-CN) 1579 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 4.74, 4.62 (s, 10H, *Cp*), 4.44, 4.13 (s, 6H, NMe_2).

*2.3 Synthesis of cis-[Fe_2{μ-CN(Me)(Xyl)}(μ-CO)(CO)(NCSMe)$(Cp)_2$][CF_3SO_3] (**3**).*

A solution of *cis*-[Fe_2{μ-CN(Me)(Xyl)}(μ-CO)(CO)(NCS)$(Cp)_2$] (131 mg, 0.260 mmol) in CH_2Cl_2 (8 mL) was treated with CF_3SO_3Me (0.030 mL, 0.26 mmol), and the solution stirred for 30 minutes at room temperature. Then, the mixture was filtered on a celite pad, and the solvent was removed under reduced pressure. The residue was washed with diethyl ether (2 x 10 mL), yielding a brown powder.

cis-**3** Yield 150.0 mg (87 %). Anal. Calcd. For $C_{25}H_{25}F_3Fe_2N_2O_5S_2$: C, 45.07; H, 3.78; N, 4.20. Found: C, 45.15; H, 3.81; N, 4.10. IR (CH_2Cl_2, 293 K): ν(CO) 1989 (vs), 1810 (s); ν(μ-CN) 1507 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K) Isomer α: δ 7.42-7.29 (m, 3H, $Me_2C_6H_3$), 5.04, 4.51 (s, 10H, *Cp*), 4.79 (s, 3H, NMe), 2.70, 2.13 (s, 6H, $Me_2C_6H_3$), 2.42 (s, 3H, SMe); Isomer β: δ 7.42-7.29 (m, 3H, $Me_2C_6H_3$), 5.17, 4.34 (s, 10H, *Cp*), 4.50 (s, 3H, NMe), 2.71, 2.07 (s, 6H, $Me_2C_6H_3$), 2.35 (s, 3H, SMe). Isomer ratio = 2. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) Isomer α: δ 337.2 (μ-*C*), 263.4 (μ-*C*O), 210.9 (CO), 147.9 (*C*ipso Xyl), 133.1, 132.0, 129.9, 129.1, 128.9 (*C*-Me + *C*H Xyl), 124.1 (N*C*S), 88.1, 87.7 (*Cp*), 54.2 (N*Me*), 18.7, 17.4 ($Me_2C_6H_3$), 16.7 (SMe); Isomer β: 336.5 (μ-*C*), 264.1 (μ-*C*O), 210.4 (CO), 148.0 (*C*ipso Xyl), 133.5, 132.4, 129.8, 129.0 (*C*-Me + *C*H Xyl), 123.7 (N*C*S), 89.1, 86.8 (*Cp*), 55.2 (N*Me*), 18.9, 17.8, ($Me_2C_6H_3$), 16.6 (SMe). ESI-MS (ES^+): 517 (M^+, 65%), 444 (M^+-NCSMe, 100%) m/z.

*2.4 Synthesis of [M_2{μ-CN(Me)(R)}(μ-CO)(CO)(NCO)$(Cp)_2$] (M= Fe, R= Me, **4a**; M= Ru R= Xyl, **4b**; M= Ru, R= Me, **4c**).*

NaNCO (500 mg, 7.69 mmol) was added to a solution of [M_2{CN(Me)(R)}(μ-CO)(CO)(CH_3CN)$(Cp)_2$][TfO] (0.230 mmol) in THF (15 ml), and the resulting suspension was heated at reflux temperature for 3 hours. Hence, the solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2 and chromatographed through Al_2O_3. A fraction corresponding to the final product [M_2{μ-CN(Me)(R)}(μ-CO)(CO)(NCO)$(Cp)_2$] was obtained using MeCN as eluent.

4a Yield 69.2 mg (76 %). Anal. Calcd. For $C_{16}H_{16}Fe_2N_2O_3$: C, 48.52; H, 4.07; N, 7.08. Found: C, 48.23; H, 4.21; N, 6.89. IR (CH_2Cl_2, 293 K): ν(NCO) 2237 (vs); ν(CO) 1980 (vs), 1803 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 4.77, 4.63 (s, 10H, *Cp*), 4.64, 4.23 (s, 6H, NMe_2).

4b Yield 104.7 mg (79 %). Anal. Calcd. For $C_{23}H_{22}N_2O_3Ru_2$: C, 47.91; H, 3.85; N, 4.86. Found: C, 47.46; H, 3.99; N, 4.65. IR (CH_2Cl_2, 293 K): ν(NCO) 2236 (s); ν(CO) 1978 (vs), 1802 (s); ν(μ-CN) 1519 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 7.29-7.19 (m, 3H, $Me_2C_6H_3$), 5.16, 4.84 (s, 10H, *Cp*), 4.25 (s, 3H, N*Me*), 2.40, 2.29 (s, 6H, $Me_2C_6H_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 313.1 (μ-*C*N), 235.8 (μ-*C*O), 200.1 (*C*O), 147.9 (*C*ipso Xyl), 133.7, 132.6 (*C*-Me Xyl), 129.9, 128.4, 128.1 (*C*H Xyl), 128.9 (N*C*O), 88.5, 87.5 (*Cp*), 51.5 (N*Me*), 18.3, 17.5 ($Me_2C_6H_3$).

4c Yield 92.7 mg (83 %). Anal. Calcd. For $C_{16}H_{16}N_2O_3Ru_2$: C, 39.51; H, 3.32; N, 5.76. Found: C, 39.89; H, 3.68; N, 5.91. IR (CH_2Cl_2, 293 K): ν(NCO) 2237 (s); ν(CO) 1977 (vs), 1802 (s); ν(μ-CN) 1589 (m), 1564 (ms) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 5.20, 5.02 (s, 10H, *Cp*), 4.02, 3.98 (s, 6H, N*Me*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 307.0 (μ-*C*N), 236.2 (μ-*C*O), 199.3 (*C*O), 127.2 (N*C*O), 88.5, 87.1 (*Cp*), 52.4, 51.1 (N*Me*$_2$).

2.5 Synthesis of [M$_2${μ-CN(Me)(R)}(μ-CO)(CO)(N$_3$)(Cp)$_2$] (M= Fe, R= Xyl, ***5a****; M= Fe R= Me,* ***5b****; M= Ru, R= Xyl,* ***5c****).*

NaN_3 (500 mg, 7.69 mmol) was added to a solution of [M_2{CN(Me)(R)}(μ-CO)(CO)(CH_3CN)(Cp)$_2$][TfO] (0.230 mmol) in THF (15 ml), and the resulting suspension was heated at reflux temperature for 3 hours. Hence, the solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2 and chromatographed through Al_2O_3. The product [M_2{μ-CN(Me)(R)}(μ-CO)(CO)(NCO)(Cp)$_2$] was obtained using THF as eluent.

5a Yield 78.7 mg (70 %). Anal. Calcd. For $C_{22}H_{22}Fe_2N_4O_2$: C, 54.36; H, 4.56; N, 11.52. Found: C, 54.57; H, 4.01; N, 11.23. IR (CH_2Cl_2, 293 K): ν(N_3) 2033 (vs); ν(CO) 1980 (s), 1800 (br) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K) Isomer α: δ 7.40-7.26 (m, 3H, $Me_2C_6H_3$), 4.87 (s, 3H, N*Me*), 4.80, 4.30 (s, 10H, *Cp*), 2.71, 2.23 (s, 6H, *Me*$_2$C$_6$H$_3$); Isomer β: δ 7.40-7.26 (m, 3H, $Me_2C_6H_3$), 5.04 (s, 3H, N*Me*), 4.85, 4.21 (s, 10H, *Cp*), 2.61, 2.42 (s, 6H, *Me*$_2$C$_6$H$_3$). α/β= 10. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) Isomer α: δ 342.5 (μ-*C*N), 266.1 (μ-*C*O), 211.3 (*C*O), 148.4-128.5 (Xyl), 86.6 (*Cp*), 52.3 (N*Me*), 18.6, 17.6 (*Me*$_2$C$_6$H$_3$); Isomer β: 86.5 (*Cp*), 52.4 (N*Me*).

5b Yield 59.2 mg (65 %). Anal. Calcd. For $C_{15}H_{16}Fe_2N_4O_2$: C, 45.49; H, 4.07; N, 14.15. Found: C, 45.11; H, 4.23; N, 14.45. IR (CH_2Cl_2, 293 K): ν(N_3) 2030 (vs); ν(CO) 1976 (vs), 1806 (s); ν(μ-CN) 1578 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 4.74, 4.63 (s, 10H, *Cp*), 4.66, 4.24 (s, 6H, N*Me*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 89.1, 86.6 (*Cp*), 52.8, 51.6 (N*Me*$_2$).

5c Yield 99.5 mg (75 %). Anal. Calcd. For $C_{22}H_{22}N_4O_2Ru_2$: C, 45.83; H, 3.85; N, 9.72. Found: C, 46.15; H, 3.61; N, 9.91. IR (CH_2Cl_2, 293 K): ν(N_3) 2033 (vs); ν(CO) 1974 (s), 1800 (s); ν(μ-CN) 1512 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 7.29-7.20 (m, 3H, $Me_2C_6H_3$), 5.21, 4.83 (s, 10H, *Cp*), 4.30 (s, 3H, N*Me*), 2.39, 2.32 (s, 6H, *Me*$_2$C$_6$H$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 312.1 (μ-*C*N), 237.0 (μ-*C*O), 200.3 (*C*O), 147.9 (*C*ipso Xyl), 133.7, 132.6 (*C*-Me Xyl), 129.7, 128.3, 128.0 (*C*H Xyl), 88.5, 87.8 (*Cp*), 51.3 (N*Me*), 18.2, 17.5 (*Me*$_2$C$_6$H$_3$).

2.6 Synthesis of [M$_2${μ-CN(Me)(R)}(μ-CO)(CO){N$_3$C$_2$(CO$_2$Me)$_2$}(Cp)$_2$] (M= Fe, R= Xyl, ***6a****; M= Fe R= Me,* ***6b****; M= Ru, R= Xyl,* ***6c****).*

A solution containing $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(N_3)(Cp)_2]$ (0.411 mmol) and $MeO_2CC{\equiv}CCO_2Me$ (0.2 ml, 1.63 mmol) in THF (15 ml) was heated at reflux temperature for 3 hours and, then, the solvent was removed under reduced pressure. Hence, the residue was washed with petroleum ether (2x20 ml), dissolved in CH_2Cl_2 and chromatographed through Al_2O_3. The final product was obtained as an orange-brown fraction using THF as eluent.

6a Yield 206.6 mg (70 %). Anal. Calcd. For $C_{28}H_{28}Fe_2N_4O_6$: C, 53.53; H, 4.49; N, 8.92. Found: C, 53.89; H, 4.06; N, 8.68. IR (CH_2Cl_2, 293 K): ν(CO) 1985 (vs), 1806 (s); $\nu(CO_2Me)$ 1734 (s); ν(μ-CN) 1507 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 7.31-7.23 (m, 3H, $Me_2C_6H_3$), 4.96 (s, 3H, N*Me*), 4.85, 4.28 (s, 10H, *Cp*), 3.72 (s, 6H, CO_2Me), 2.68, 2.15 (s, 6H, $Me_2C_6H_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 340.4 (μ-*C*N), 265.9 (μ-*C*O), 210.6 (*C*O), 162.1 (CO_2Me), 148.9 (*C*ipso Xyl), 140.5 (N_3C_2), 134.8, 132.6 (*C*-Me Xyl), 130.2, 128.3, 128.1 (*C*H Xyl), 87.3, 86.9 (*Cp*), 53.2 (N*Me*), 51.5 (CO_2Me), 18.6, 17.1 ($Me_2C_6H_3$).

6b Yield 168.1 mg (76 %). Anal. Calcd. For $C_{21}H_{22}Fe_2N_4O_6$: C, 46.87; H, 4.12; N, 10.41. Found: C, 47.05; H, 3.98; N, 10.07. IR (CH_2Cl_2, 293 K): ν(CO) 1983 (vs), 1806 (s); $\nu(CO_2Me)$ 1727 (s); ν(μ-CN) 1577 (w), 1551 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 4.73, 4.71 (s, 10H, *Cp*), 4.68, 4.11 (s, 6H, NMe_2), 3.69 (s, 6H, CO_2Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 334.3 (μ-*C*N), 265.9 (μ-*C*O), 210.0 (*C*O), 162.1 (CO_2Me), 140.2 (N_3C_2), 87.0, 86.9 (*Cp*), 53.3, 52.2 (NMe_2), 51.6 (CO_2Me).

6c Yield 254.4 mg (86 %). Anal. Calcd. For $C_{28}H_{28}N_4O_6Ru_2$: C, 46.79; H, 3.93; N, 7.80. Found: C, 46.24; H, 4.11; N, 7.99. IR (CH_2Cl_2, 293 K): ν(CO) 1979 (vs), 1804 (s); $\nu(CO_2Me)$ 1738 (sh), 1713 (vs); ν(μ-CN) 1519 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 7.31-7.20 (m, 3H, $Me_2C_6H_3$), 5.33, 4.85 (s, 10H, *Cp*), 4.44 (s, 3H, N*Me*), 3.83 (s, 6H, CO_2Me), 2.44, 2.22 (s, 6H, $Me_2C_6H_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 311.4 (μ-*C*N), 236.3 (μ-*C*O), 199.0 (*C*O), 162.2 (CO_2Me), 148.3 (*C*ipso Xyl), 139.7 (N_3C_2), 134.3, 132.3 (*C*-Me Xyl), 129.9, 128.2, 127.7 (*C*H Xyl), 88.6, 88.1 (*Cp*), 52.1 (N*Me*), 51.6 (CO_2Me), 18.4, 17.1 ($Me_2C_6H_3$).

*2.7 Synthesis of $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{N_3C_2(H)(CO_2Me)\}(Cp)_2]$ (M= Fe, R= Me, **7a**; M= Ru, R= Xyl, **7b**).*

A solution containing $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(N_3)(Cp)_2]$ (0.240 mmol) and $HC{\equiv}CCO_2Me$ (0.1 ml, 1.12 mmol) in THF (15 ml) was heated at reflux temperature for 3 hours and, then, the solvent was removed under reduced pressure. Hence, the residue was washed with petroleum ether (2x20 ml), dissolved in CH_2Cl_2 and chromatographed through Al_2O_3. The final product was obtained as an orange-brown fraction using THF as eluent.

7a Yield 93.5 mg (81 %). Anal. Calcd. For $C_{19}H_{20}Fe_2N_4O_4$: C, 47.53; H, 4.20; N, 11.67. Found: C, 47.86; H, 4.01; N, 11.12. IR (CH_2Cl_2, 293 K): ν(CO) 1982 (vs), 1805 (s); $\nu(CO_2Me)$ 1721 (s); ν(μ-

CN) 1576 (ms), 1505 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K) Major isomer: δ 7.56 (s, 1H, C*H*), 4.82, 4.78 (s, 10H, *Cp*), 4.70, 4.21 (s, 6H, N*Me*$_2$), 3.73 (s, 3H, CO_2*Me*); Minor isomer: δ 7.72 (s, 1H, C*H*), 4.91, 4.81 (s, 10H, *Cp*), 4.70, 4.21 (s, 6H, N*Me*$_2$), 3.76 (s, 3H, CO_2*Me*). Major/Minor = 2. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) Major isomer: δ 334.3 (μ-*C*N), 266.6 (μ-*C*O), 210.3 (*C*O), 162.4 (*C*O_2Me), 138.2 (N_3CH*C*CO_2Me), 137.6 (*C*H), 87.0, 86.9 (*Cp*), 53.2, 52.2 (N*Me*$_2$), 50.8 (CO_2*Me*); Minor isomer: δ 332.5 (μ-*C*N), 270.7 (μ-*C*O), 209.6 (*C*O), 162.2 (*C*O_2Me), 139.7 (N_3CH*C*CO_2Me), 139.4 (*C*H), 87.1, 86.7 (*Cp*), 53.5, 52.8 (N*Me*$_2$), 50.9 (CO_2*Me*).

7b Yield 128.7 mg (81 %). Anal. Calcd. For $C_{26}H_{26}N_4O_4Ru_2$: C, 47.27; H, 3.97; N, 8.48. Found: C, 47.65; H, 3.68; N, 8.89. IR (CH_2Cl_2, 293 K): ν(CO) 1978 (s), 1803 (s); ν(CO_2Me) 1712 (s); ν(μ-CN) 1520 (ms), 1505 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K) Major isomer: δ 7.86 (s, 1H, C*H*), 7.27-7.22 (m, 3H, Me_2C_6*H*$_3$), 5.25, 4.86 (s, 10H, *Cp*), 4.52 (s, 3H, N*Me*), 3.83 (s, 3H, CO_2*Me*), 2.46, 2.18 (s, 6H, *Me*$_2C_6H_3$); Minor isomer: δ 7.79 (s, 1H, C*H*), 7.27-7.22 (m, 3H, Me_2C_6*H*$_3$), 5.33, 4.86 (s, 10H, *Cp*), 4.48 (s, 3H, N*Me*), 3.79 (s, 3H, CO_2*Me*), 2.46, 2.19 (s, 6H, *Me*$_2C_6H_3$). Major/Minor = 2. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) Major isomer: δ 310.7 (μ-*C*N), 240.1 (μ-*C*O), 199.1 (*C*O), 162.9 (*C*O_2Me), 148.5 (*C*ipso Xyl), 139.5 (*C*H), 137.3 (N_3CH*C*CO_2Me), 134.5, 132.3 (*C*-Me Xyl), 130.0-127.8 (*C*H Xyl), 88.7, 88.0 (*Cp*), 52.5 (N*Me*), 51.0 (CO_2*Me*), 18.3, 17.3 (*Me*$_2C_6H_3$); Minor isomer: δ 311.9 (μ-*C*N), 237.3 (μ-*C*O), 199.5 (*C*O), 162.8 (*C*O_2Me), 148.5 (*C*ipso Xyl), 139.4 (*C*H), 138.1 (N_3CH*C*CO_2Me), 134.5, 132.5 (*C*-Me Xyl), 130.0-127.8 (*C*H Xyl), 88.6, 88.2 (*Cp*), 52.0 (N*Me*), 51.0 (CO_2*Me*), 18.3, 16.9 (*Me*$_2C_6H_3$).

*2.8 Synthesis of [Fe$_2${μ-CN(Me)(Xyl)}(μ-CO)(CO){N_3C_2(H)(CN)}(Cp)$_2$], **8**.*

A solution containing [Fe_2{μ-CN(Me)(Xyl)}(μ-CO)(CO)(N_3)(Cp)$_2$] (75.1 mg, 0.154 mmol) and (NC)(H)C≡C(H)(CN) (34.1 mg, 0.437 mmol) in THF (6 ml) was heated at reflux temperature for 5 hours and, then, the solvent was removed under reduced pressure. Hence, the residue was washed with petroleum ether (2x20 ml), dissolved in CH_2Cl_2 and chromatographed through Al_2O_3. The final product was obtained as an orange-brown fraction using THF as eluent.

8 Yield 67.8 mg (82 %). Anal. Calcd. For $C_{25}H_{23}Fe_2N_5O_2$: C, 55.90; H, 4.32; N, 13.04. Found: C, 55.59; H, 4.54; N, 13.15. IR (CH_2Cl_2, 293 K): ν(CN) 2232 (ms); ν(CO) 1986 (vs), 1805 (s); ν(μ-CN) 1509 (ms), 1505 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K) Major isomer: δ 7.74 (s, 1H, C*H*), 7.31-7.21 (m, 3H, Me_2C_6*H*$_3$), 5.11 (s, 3H, N*Me*), 4.74, 4.29 (s, 10H, *Cp*), 2.69, 2.03 (s, 6H, *Me*$_2C_6H_3$); Minor isomer: δ 7.46 (s, 1H, C*H*), 7.31-7.21 (m, 3H, Me_2C_6*H*$_3$), 4.96 (s, 3H, N*Me*), 4.81, 4.28 (s, 10H, *Cp*), 2.68, 2.08 (s, 6H, *Me*$_2C_6H_3$). Major/Minor = 1.1. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) Major isomer: δ 339.2 (μ-*C*N), 270.9 (μ-*C*O), 210.1 (*C*O), 148.9 (*C*ipso Xyl), 140.9 (*C*H), 134.5, 132.4 (*C*-Me Xyl), 130.4-128.2 (*C*H Xyl), 118.5 (*C*N), 114.4 (N_3CH*C*CN), 87.2, 86.9 (*Cp*), 53.9 (N*Me*),

18.6, 17.2 ($Me_2C_6H_3$); Minor isomer: δ 340.9 (μ-*C*N), 266.7 (μ-*C*O), 210.8 (*C*O), 149.0 (*C*ipso Xyl), 139.2 (*C*H), 134.5, 132.6 (*C*-Me Xyl), 130.4-128.2 (*C*H Xyl), 119.4 (*C*N), 114.5 (N_3CHCCN), 87.3, 86.0 (*Cp*), 53.1 (N*Me*), 18.6, 16.9 ($Me_2C_6H_3$).

*2.9 Synthesis of [Fe_2\{μ-CN(Me)(Xyl)\}(μ-CO)(CO)\{$N_3(Me)C_2(CO_2Me)_2$\}$(Cp)_2$][CF_3SO_3], **9**.*

CF_3SO_3Me (0.1 ml, 0.884 mmol) was added to a solution of **6a** (200.0 mg, 0.279 mmol) in CH_2Cl_2 (6 ml); after stirring at room temperature for 30 minutes, the solvent was removed under reduced pressure and the residue washed with Et_2O (2x10 ml).

9 Yield 222.6 mg (92 %). Anal. Calcd. For $C_{30}H_{31}F_3Fe_2N_4O_9S$: C, 41.55; H, 3.60; N, 6.46. Found: C, 41.92; H, 3.47; N, 6.31. IR (CH_2Cl_2, 293 K): ν(CO) 1982 (vs), 1808 (s); ν(CO_2Me) 1745 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 7.25 (m, 3H, $Me_2C_6H_3$), 5.06 (s, 3H, N*Me*), 4.90, 4.28 (s, 10H, *Cp*), 3.98 (s, 3H, N_3Me), 3.80 (s, 6H, CO_2Me), 2.62, 2.15 (s, 6H, $Me_2C_6H_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 330.4 (μ-*C*N), 266.9 (μ-*C*O), 210.7 (*C*O), 155.8 (CO_2Me), 148.9 (*C*ipso Xyl), 133.6, 132.8, 132.7 (*C*-Me Xyl + N_3C_2), 130.0, 128.8, 128.7 (*C*H Xyl), 88.3, 87.2 (*Cp*), 54.6, 53.7 (N*Me* + CO_2Me), 39.5 (N_3Me), 18.7, 16.9 ($Me_2C_6H_3$).

*2.10 Synthesis of [M_2\{μ-CN(Me)(R)\}(μ-CO)(CO)\{$N_3(Me)C_2(H)(CO_2Me)$\}$(Cp)_2$][CF_3SO_3] (M = Fe, R = Me, **10a**; M = Ru, R = Xyl, **10b**).*

CF_3SO_3Me (0.1 ml, 0.884 mmol) was added to a solution of **7** (0.300 mmol) in CH_2Cl_2 (6 ml); after stirring at room temperature for 30 minutes, the solvent was removed under reduced pressure and the residue washed with Et_2O (2x10 ml).

10a Yield 172.0 mg (89 %). Anal. Calcd. For $C_{21}H_{23}F_3Fe_2N_4O_7S$: C, 39.15; H, 3.60; N, 8.70. Found: C, 39.03; H, 3.82; N, 8.46. IR (CH_2Cl_2, 293 K): ν(CO) 1983 (vs), 1799 (s); ν(CO_2Me) 1742 (m), 1718 (m); ν(μ-CN) 1581 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 8.03 (s, 1H, C*H*), 4.96, 4.79 (s, 10H, *Cp*), 4.82, 4.30 (s, 6H, NMe_2), 4.03 (s, 3H, N_3Me), 3.84 (s, 3H, CO_2Me).

10b Yield 235.0 mg (95 %). Anal. Calcd. For $C_{28}H_{29}F_3N_4O_7Ru_2S$: C, 40.78; H, 3.54; N, 6.80. Found: C, 40.46; H, 3.74; N, 7.01. IR (CH_2Cl_2, 293 K): ν(CO) 1978 (vs), 1806 (s); ν(CO_2Me) 1746 (s); ν(μ-CN) 1528 (ms) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 8.14 (s, 1H, C*H*), 7.24-7.21 (m, 3H, $Me_2C_6H_3$), 5.34, 4.89 (s, 10H, *Cp*), 4.36 (s, 3H, N*Me*), 4.19 (s, 3H, N_3Me), 3.90 (s, 3H, CO_2Me), 2.41, 2.19 (s, 6H, $Me_2C_6H_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 310.8 (μ-*C*N), 240.0 (μ-*C*O), 200.3 (*C*O), 156.9 (CO_2Me), 148.2 (*C*ipso Xyl), 143.5 (*C*H), 130.0, 132.6 (*C*-Me Xyl), 129.9 (N_3CHCCO_2Me), 129.8, 128.8, 128.7 (*C*H Xyl), 89.6, 88.3 (*Cp*), 53.3 (N*Me*), 53.1 (CO_2Me), 38.7 (N_3Me), 18.4, 16.9 ($Me_2C_6H_3$).

*2.11 Synthesis of [Fe_2{μ-CN(Me)(Xyl)}(μ-CO)(CO){$N_3(Me)C_2(H)(CN)$}$(Cp)_2$][CF_3SO_3], **11**.*

CF_3SO_3Me (0.1 ml, 0.884 mmol) was added to a solution of **8** (190.0 mg, 0.354 mmol) in CH_2Cl_2 (6 ml); after stirring at room temperature for 30 minutes, the solvent was removed under reduced pressure and the residue washed with Et_2O (2x10 ml).

11 Yield 223.5 mg (92 %). Anal. Calcd. For $C_{27}H_{26}F_3Fe_2N_5O_5S$: C, 47.26; H, 3.82; N, 10.21. Found: C, 47.62; H, 3.67; N, 10.45. IR (CH_2Cl_2, 293 K): ν(CN) 2220 (m), ν(CO) 1986 (vs), 1818 (s); ν(μ-CN) 1522 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K) Major isomer: δ 9.13 (s, 1H, C*H*), 7.30 (m, 3H, $Me_2C_6H_3$), 4.19 (s, 3H, N*Me*), 5.07, 4.50 (s, 10H, *Cp*), 3.85 (s, 3H, N_3Me), 2.69, 2.03 (s, 6H, $Me_2C_6H_3$); Minor isomer: δ 8.37 (s, 1H, C*H*), 7.30 (m, 3H, $Me_2C_6H_3$), 5.14 (s, 3H, N*Me*), 4.98, 4.38 (s, 10H, *Cp*), 4.34 (s, 3H, N_3Me), 2.66, 2.11 (s, 6H, $Me_2C_6H_3$). Major/Minor = 1.2. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) Major isomer: δ 336.1 (μ-*C*N), 265.6 (μ-*C*O), 210.7 (*C*O), 148.3 (*C*ipso Xyl), 134.8, 132.6 (*C*-Me Xyl), 132.3 (N_3CHCCN), 130.1-128.8 (*C*H Xyl), 118.7 (*C*H), 117.7 (*C*N), 88.2, 86.8 (*Cp*), 54.2 (N*Me*), 41.0 (N_3Me), 18.3, 17.0 ($Me_2C_6H_3$); Minor isomer: δ 338.3 (μ-*C*N), 261.7 (μ-*C*O), 210.7 (*C*O), 147.7 (*C*ipso Xyl), 136.7, 132.8 (*C*-Me Xyl), 131.8 (N_3CHCCN), 130.1-128.8 (*C*H Xyl), 119.2 (*C*H), 116.8 (*C*N), 88.3, 88.2 (*Cp*), 54.0 (N*Me*), 40.3 (N_3Me), 18.5, 16.9 ($Me_2C_6H_3$).

2.12 Crystallography

Compounds *trans*-**2b**, **4b·CH_2Cl_2**, **5a**, **6b·0.5CH_2Cl_2** and **8·CH_2Cl_2** were crystallized from CH_2Cl_2/ petroleum ether at –20 ºC. Crystal data were collected on a Bruker AXS SMART 2000 CCD diffractometer using Mo-Kα radiation. Intensity data were measured over full diffraction spheres using 0.3° wide ω scans, crystal-to-detector distance 5.2 cm. Cell dimensions and orientation matrixes were initially determined from least-squares refinements on reflections measured in 3 sets of 20 exposures collected in three different ω regions and eventually refined against all reflections. The software SMART [13] was used for collecting frames of data, indexing reflections and determinations of lattice parameters. The collected frames were then processed for integration by the software SAINT and empirical absorption corrections were applied with SADABS [14]. The structure was solved by direct methods and refined by full-matrix least-squares based on all data using F^2 [15]. Crystal data are listed in Table 1. Non-H atoms were refined anisotropically, unless otherwise stated. H-atoms were placed in calculated positions, and treated isotropically using the 1.2 fold U_{iso} value of the parent atom except methyl protons, which were assigned the 1.5 fold U_{iso} value of the parent C-atoms. One Cp ligand in *trans*-**3b** and the CH_2Cl_2 molecule in **4b·CH_2Cl_2** are disordered. Disordered atomic positions were split and refined

isotropically using similar distance and similar *U* restraints and one occupancy parameter per disordered group.

Table 1

Crystal data and experimental details.

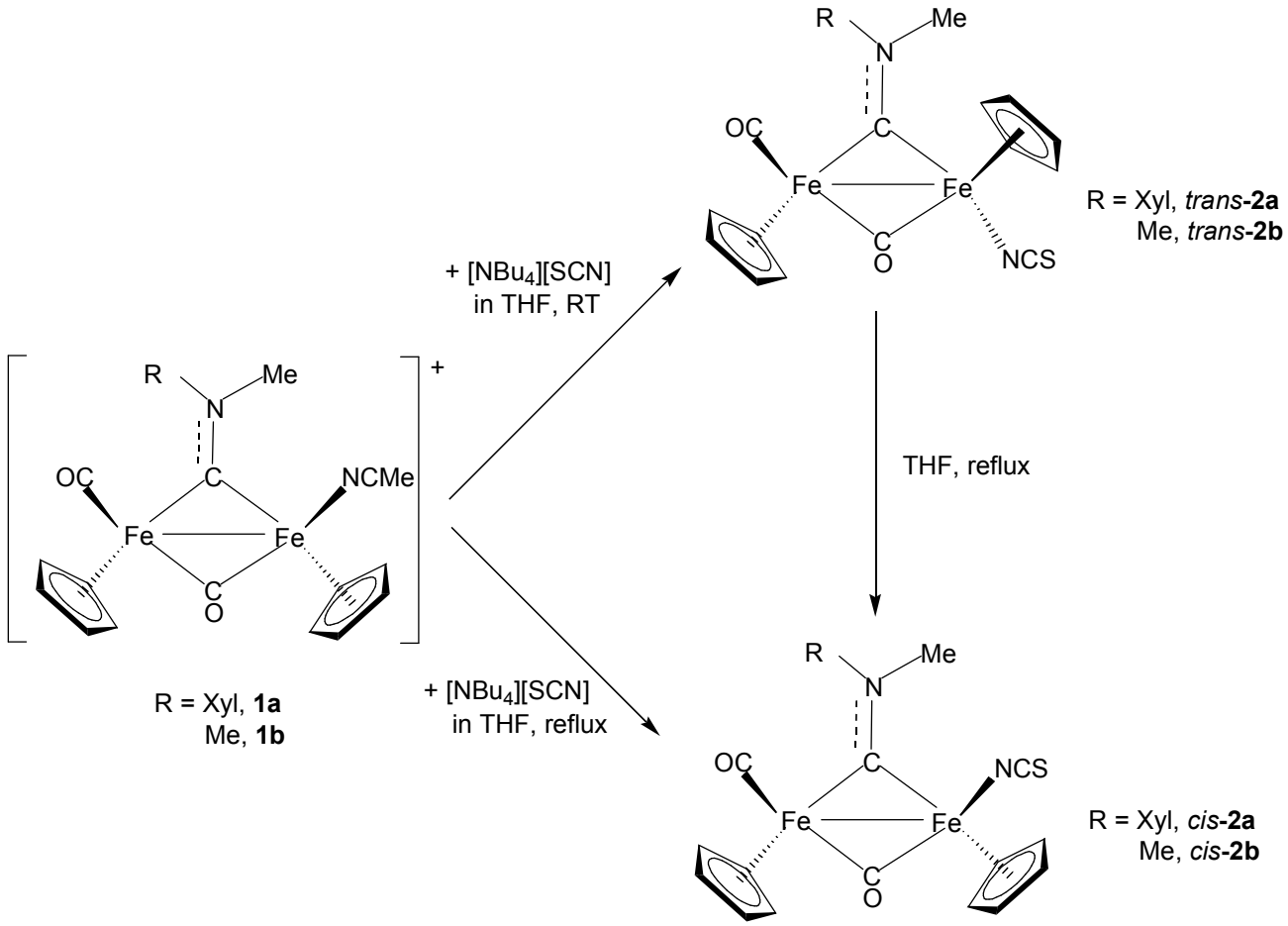
Complex	*trans*-**2b**	**4b·CH_2Cl_2**	**5a**	**6b·0.5CH_2Cl_2**	**8·CH_2Cl_2**
Formula	$C_{16}H_{16}Fe_2N_2O_2S$	$C_{24}H_{24}Cl_2N_2O_3Ru_2$	$C_{22}H_{22}Fe_2N_4O_2$	$C_{21.5}H_{23}ClFe_2N_4O_6$	$C_{26}H_{25}Cl_2Fe_2N_5O_2$
Fw	412.07	661.49	486.14	580.59	622.11
T, K	293(2)	293(2)	293(2)	293(2)	100(2)
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	*P*bca	$P2_1$/n	$P2_1$/c	$P\bar{1}$	$P2_1$/n
a, Å	13.5828(5)	13.112(3)	9.0971(4)	9.0434(18)	13.370(3)
b, Å	14.7056(6)	13.975(3)	12.1634(5)	14.838(3)	12.149(2)
c, Å	16.8850(7)	13.879(3)	18.6203(8)	18.788(4)	16.050(3)
α, °	90	90	90	81.12(3)	90
β, °	90	93.31(3)	93.5230(10)	86.34(3)	96.04(3)
γ, °	90	90	90	73.67(3)	90
Cell Volume, $Å^3$	3372.7(2)	2538.9(9)	2056.47(15)	2389.8(8)	2592.6(9)
Z	8	4	4	4	4
D_c, g cm^{-3}	1.623	1.731	1.570	1.614	1.594
μ, mm^{-1}	1.853	1.428	1.437	1.371	1.360
F(000)	1680	1312	1000	1188	1272
Crystal size, mm	0.25x0.22x0.14	0.27x0.23x 0.16	0.36x0.28x0.16	0.24x0.29x0.13	0.36x0.27x0.18
θ limits, °	2.37-26.37	2.07-25.02	2.00-27.48	1.10-25.03	1.89-27.10
Reflections collected	31402	21941	21992	21312	26853
Independent reflections	3441 [R_{int} = 0.0792]	4487 [R_{int} = 0.0560]	4721 [R_{int} = 0.0587]	8442 [R_{int} = 0.0680]	5716 [R_{int} = 0.0662]
Data / restraints /	3441 / 26 / 206	4487 / 11 / 299	4721 / 0 / 274	8442 / 159 / 630	5716 / 1 / 337

parameters					
Goodness on fit on F^2	1.050	1.055	1.053	0.930	1.063
R1 ($I > 2\sigma(I)$)	0.0475	0.0427	0.0429	0.0520	0.0454
WR2 (all data)	0.1402	0.1237	0.1169	0.1302	0.1193
Largest diff. peak and hole, e $Å^{-3}$	0.755 / -0.600	1.076 / -0.793	0.457 / -0.340	0.603 / -0.482	0.855 / -0.649

3. Results and Discussion

The MeCN ligand in the μ-aminocarbyne complexes $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(MeCN)(Cp)_2][SO_3CF_3]$ (R= Xyl, **1a**; Me, **1b**) is almost quantitatively replaced by NCS^- after stirring **1** in THF for 3 hours in the presence of an excess of $[NBu_4][SCN]$ (Scheme 1). The new complexes *trans*-$[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NCS)(Cp)_2]$□ (R= Xyl, *trans*-**2a**; Me, *trans*-**2b**) are, hence, obtained in good yields (71-76 %) after column chromatography, and they have been fully characterised by IR and NMR spectroscopy.

Scheme 1



The molecular structure of *trans*-**2b** has been, also, determined by X-ray crystallography (Figure 1 and Table 2). The Cp ligands adopt a *trans* geometry relative to the mean plane determined by the $Fe_2(\mu\text{-}C)_2$ core. This is quite unusual, since most of the structures reported for diiron complexes containing a bridging aminocarbyne ligand show a *cis* geometry of the Cp ligands [8-10]. The C(13)-N(1) interaction [1.297(5) Å] exhibits a considerably double bond character, suggesting that the μ-aminocarbyne ligand can be alternatively described as a μ-iminium ligand. The Fe(1)-N(2) interaction [1.932(3) Å] indicates a π-contribution to the bond; in agreement with this, the Fe(1)-N(2)-C(16)-S(1) unit is almost linear [bond angles Fe(1)-N(2)-C(16) 169.7(3) and N(2)-C(16)-S(1) 178.4(4)°] and N(2) and C(16) exhibit an almost perfect sp hybridisation. This linear arrangement of the atoms perfectly agrees with a N-coordinated NCS^- ligand [16]. Interestingly, the mononuclear complex $[Fe(Cp)(CO)_2(NCS)]$ exists in both the N- and S-bonded isomeric forms [17], where the N-bonded isomer is the thermodynamically more stable. The NMR data for *trans*-**2a,b** show the presence in solution of only one species, indicating the complete absence of linkage isomerism.

Figure 1

Molecular structure of *trans*-**2b**, with key atoms labelled (all H atoms have been omitted). Displacement ellipsoids are at 30% probability level.

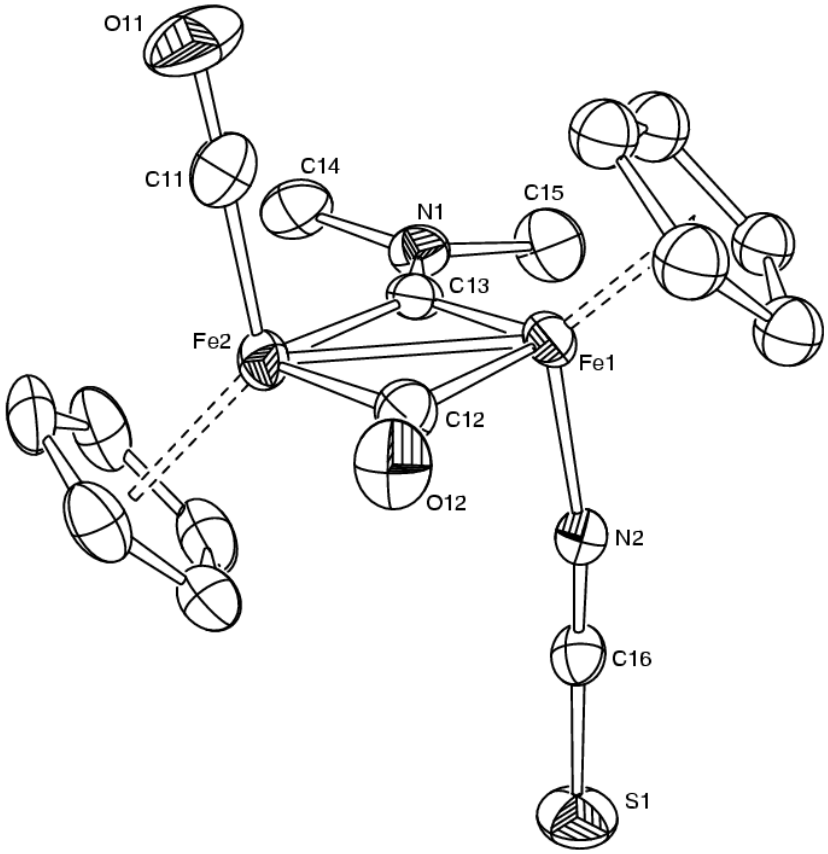


Table 2

Selected bond lengths (Å) and angles (°) for complex *trans*-**2b**.

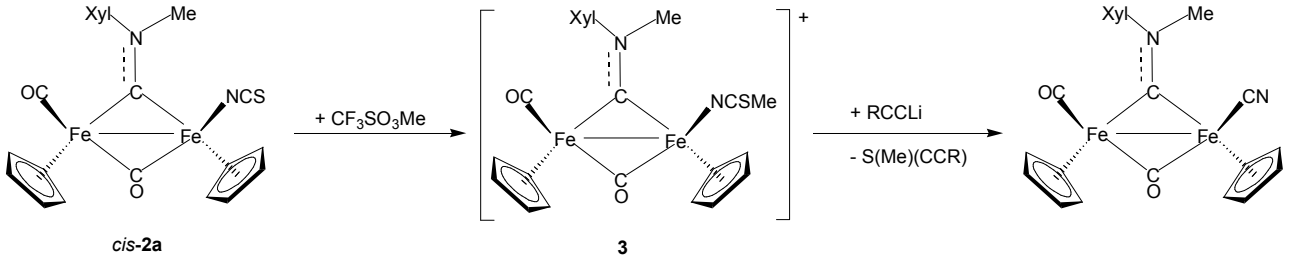
Fe(1)-Fe(2)	2.518(1)	Fe(1)-N(2)	1.932(3)
Fe(2)-C(11)	1.754(5)	N(2)-C(16)	1.151(5)
Fe(1)-C(12)	1.880(4)	C(16)-S(1)	1.622(4)
Fe(2)-C(12)	1.974(5)	C(11)-O(11)	1.148(6)
Fe(1)-C(13)	1.855(4)	C(12)-O12)	1.170(5)
Fe(2)-C(13)	1.874(4)	C(13)-N(1)	1.297(5)
Fe(1)-C(12)-Fe(2)	81.55(18)	Fe(1)-N(2)-C(16)	169.7(3)
Fe(1)-C(13)-Fe(2)	84.96(17)	N(2)-C(16)-S(1)	178.4(4)

Complexes *trans*-**2a,b** are completely converted into *cis*-[Fe_2{μ-CN(Me)(R)}(μ-CO)(CO)(NCS)$(Cp)_2$] (R= Xyl, *cis*-**2a**; Me, *cis*-**2b**) after heating at reflux temperature in THF solution for 5 hours (Scheme 1). The isomerisation is clearly indicated by a shift of *ca.* 20 cm^{-1}

toward higher frequencies of the terminal ν(CO), whereas the other IR bands remain nearly unchanged. Also the NMR data for *trans*-**2** and *cis*-**2** are very similar as expected since they differ only for the relative position of the Cp ligands. The different arrangement of the Cp has been further supported by NOE studies; thus, NOE is mutually generated between the two Cp ligans in *cis*-**2** but not in *trans*-**2**. Complexes *cis*-**2** can be directly obtained from **1** by heating at reflux the latter in the presence of NCS^-.

Complex *cis*-**2a** reacts with CF_3SO_3Me to give *cis*-[Fe_2{μ-CN(Me)(Xyl)}(μ-CO)(CO)(NCSMe)$(Cp)_2$][CF_3SO_3], **3** (Scheme 2), as clearly indicated by the spectroscopic data (see Experimental). Addition of lithium acetylides LiCCR (R= Me, Tol) to **3** results in the elimination of S(Me)(CCR) with consequent formation of the known compound *cis*-[Fe_2{μ-CN(Me)(Xyl)}(μ-CO)(CO)(CN)$(Cp)_2$], in about 80 % yield [9b].

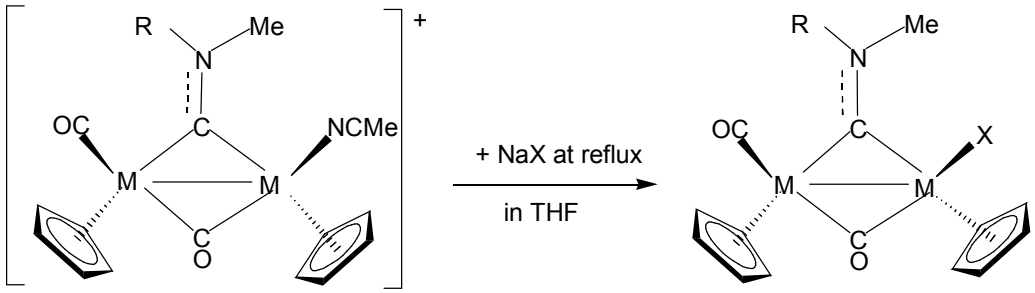
Scheme 2



cis-**2a** **3**

Similarly to what reported for the preparation of **2**, the complexes *cis*-[M_2{μ-CN(Me)(R)}(μ-CO)(CO)(NCO)$(Cp)_2$] (M = Fe, R= Me, **4a**; M = Ru, R = Xyl, **4b**; M = Ru, R = Me, **4c**) and *cis*-[M_2{μ-CN(Me)(R)}(μ-CO)(CO)$(N_3)(Cp)_2$] (M = Fe, R= Xyl, **5a**; M = Fe, R = Me, **5b**; M = Ru, R = Xyl, **5c**) are obtained by heating at reflux temperature [M_2{μ-CN(Me)(R)}(μ-CO)(CO)(MeCN)$(Cp)_2$][SO_3CF_3] (M = Fe, R= Xyl, **1a**; M = Fe, Me, **1b**; M = Ru, R = Xyl, **1c**; M = Ru, R = Me, **1d**) in THF in the presence of NaNCO and NaN_3, respectively (Scheme 3). Complexes **4-5** are obtained in good yields (65-76 %) after column chromatography.

Scheme 3



R	M	
Xyl	Fe	**1a**
Me	Fe	**1b**
Xyl	Ru	**1c**
Me	Ru	**1d**

X	R	M	
NCO	Me	Fe	**4a**
NCO	Xyl	Ru	**4b**
NCO	Me	Ru	**4c**
N_3	Xyl	Fe	**5a**
N_3	Me	Fe	**5b**
N_3	Xyl	Ru	**5c**

The molecular structures of **4b** and **5a** are reported in Figures 2 and 3, whereas the main bond lengths and bond angles are reported in Tables 3 and 4. The Cp ligands show in both the molecules a *cis* arrangement relative to the $M_2(\mu\text{-}C)_2$ core; moreover, the Xyl substituents in the μ-CN(Me)(Xyl) ligand points towards the terminal CO in both **4b** and **5a**, as previously found in analogous diiron and diruthenium complexes [10c, 18]. The metal-isocyanate linkage in **4b** is approximately linear [bond angles Ru(1)-N(2)-C(23) 167.0(5) and N(2)-C(23)-O(2) 177.8(8)°], and the C(23)-N(2) distance [1.138(8) Å] is significantly shorter than C(23)-O(2) [1.213(8) Å], implying some triple bond character for the former. This is a clear indication of the N-coordination of the NCO^- ligand, as previously demonstrated in complexes such as $[Cr(Cp)(NCO)(NO)_2]$ [19] and $[M(Cp)_2(NCO)_2]$ (M = Ti, Zr) [5]. Conversely, the azido ligand in **5a** shows a bent coordination [bond angle Fe(1)-N(2)-N(3) 120.1(3)°] and the Fe(1)-N(2) distance [2.009(3) Å] is characteristic for a σ-interaction, as found in the analogous amino complex $[Fe_2\{\mu\text{-}CN(Me)_2\}(\mu\text{-}CO)(CO)(EtNH_2)(Cp)_2][SO_3CF_3]$ [Fe-N 2.018(9) Å] [18].

Figure 2

Molecular structure of **4b**, with key atoms labelled (all H atoms have been omitted). Displacement ellipsoids are at 30% probability level.

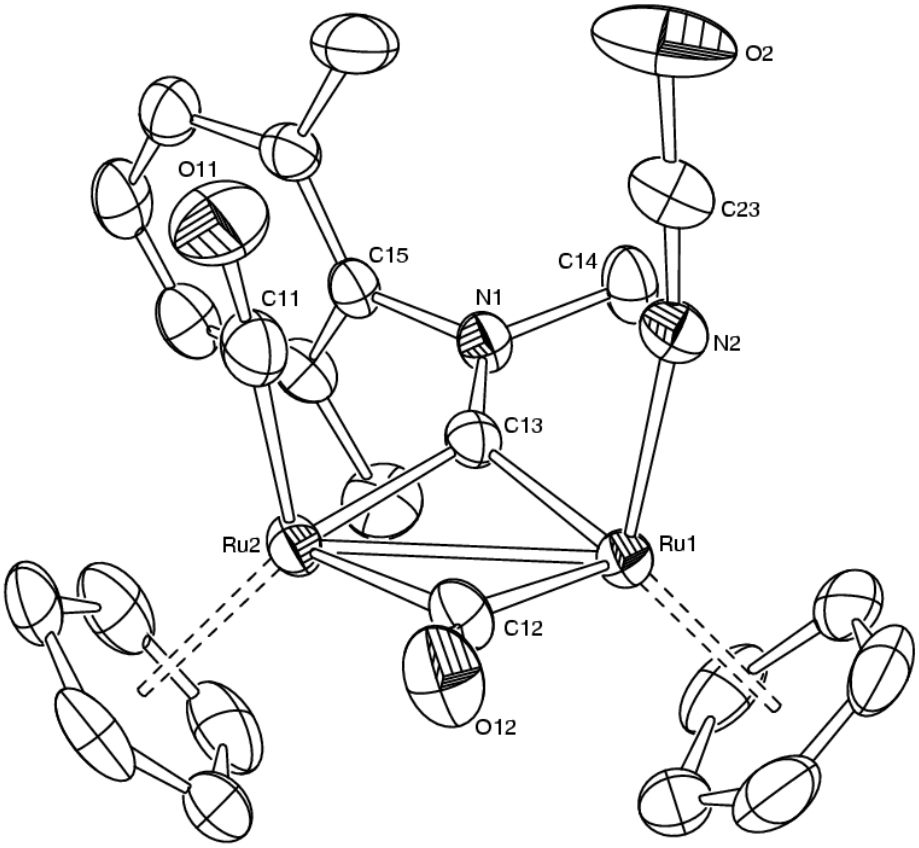


Table 3

Selected bond lengths (Å) and angles (°) for complex **4b**.

Ru(1)-Ru(2)	2.7005(8)	Ru(1)-N(2)	2.088(5)
Ru(2)-C(11)	1.850(6)	N(2)-C(23)	1.138(8)
Ru(1)-C(12)	1.981(6)	C(23)-O(2)	1.213(8)
Ru(2)-C(12)	2.108(5)	C(11)-O(11)	1.143(7)
Ru(1)-C(13)	1.940(5)	C(12)-O12)	1.166(7)
Ru(2)-C(13)	1.991(5)	C(13)-N(1)	1.304(6)
Fe(1)-C(12)-Fe(2)	82.6(2)	Fe(1)-N(2)-C(16)	167.0(35)
Fe(1)-C(13)-Fe(2)	86.8(2)	N(2)-C(16)-S(1)	177.8(8)

Figure 3

Molecular structure of **5a**, with key atoms labelled (all H atoms have been omitted). Displacement ellipsoids are at 30% probability level.

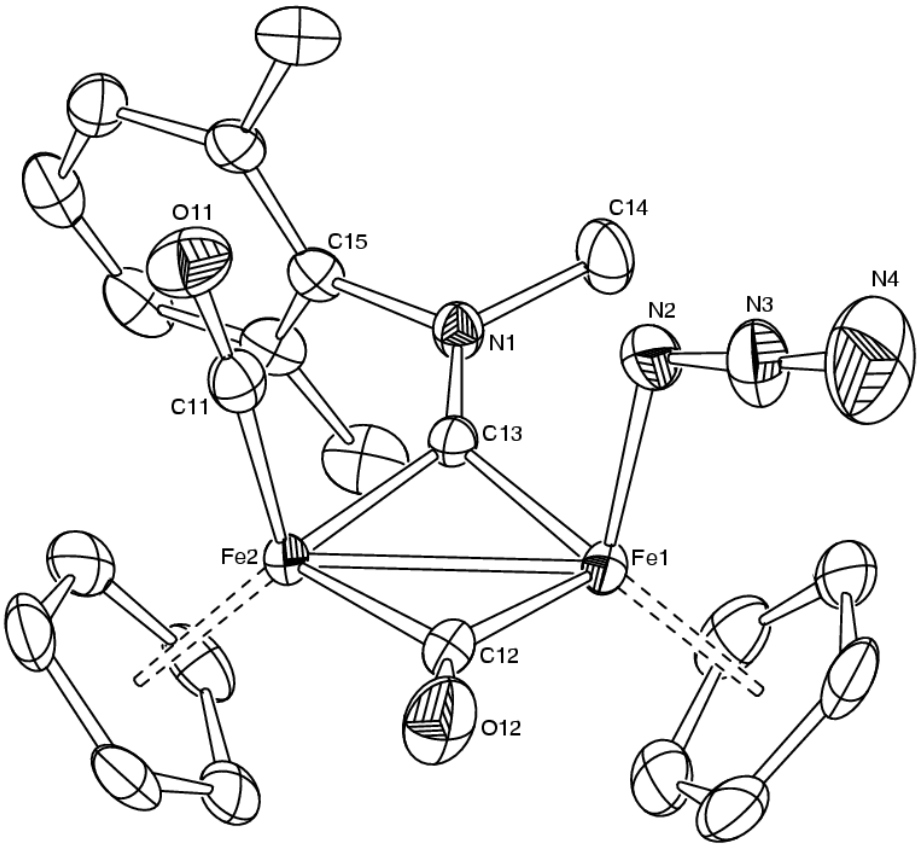


Table 4

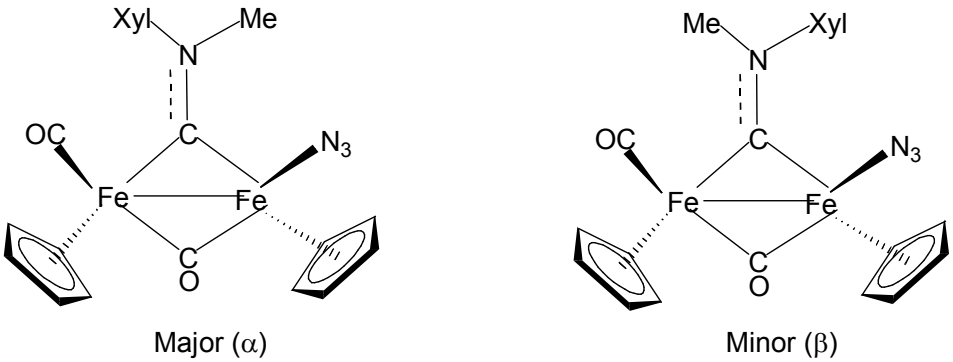
Selected bond lengths (Å) and angles (°) for complex **5a**.

Fe(1)-Fe(2)	2.4999(6)	Fe(1)-N(2)	2.009(3)
Fe(2)-C(11)	1.753(4)	N(2)-N(3)	1.187(4)
Fe(1)-C(12)	1.882(3)	N(3)-N(4)	1.161(5)
Fe(2)-C(12)	1.968(3)	C(11)-O(11)	1.143(4)
Fe(1)-C(13)	1.849(3)	C(12)-O12)	1.173(4)
Fe(2)-C(13)	1.877(3)	C(13)-N(1)	1.304(4)
Fe(1)-C(12)-Fe(2)	80.94(14)	Fe(1)-N(2)-C(16)	120.1(3)
Fe(1)-C(13)-Fe(2)	84.29(13)	N(2)-C(16)-S(1)	176.8(5)

The IR spectra of **4-5** show ν(CO) for the terminal and bridging carbonyls at *ca*. 1980 and 1800 cm^{-1}, respectively; the former data well agrees with a *cis* geometry of the Cp ligands also in solution. Moreover, complexes **4** show ν(NCO) at *ca.* 2235 cm^{-1}, whereas ν(N_3) in **5** absorbs at *ca*.

2030 cm^{-1}. The NMR spectra of **4-5** show the presence in solution of a single species, except for **5a** where a second isomer is present (major : minor = 10). This is probably due to a different orientation of the Me and Xyl substituents on the μ-CN(Me)(Xyl) ligand (Scheme 4), as previously found in analogous diiron and diruthenium μ-aminocarbyne complexes [10c, 18]. The most important feature of the ^{13}C NMR spectra is the presence of three resonances at low fields attributable to the μ-aminocarbyne carbon (δ *ca*. 340 ppm M=Fe; 310 ppm M=Ru), the μ-CO (δ *ca*. 266 ppm M=Fe; 236 ppm M=Ru) and the terminal CO ligand (δ *ca*. 211 ppm M=Fe; 200 ppm M=Ru). The carbon of the NCO ligand in **4** resonates at *ca*. 128 ppm as expected for isocyanate ligands.

Scheme 4



The azido complexes **5** react in THF solution at reflux with electron poor alkynes such as $MeO_2CC{\equiv}CCO_2Me$ and $HC{\equiv}CCO_2Me$ affording the triazolato complexes $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{N_3C_2(CO_2Me)_2\}(Cp)_2]$ (M = Fe, R= Xyl, **6a**; M = Fe, R = Me, **6b**; M = Ru, R = Xyl, **6c**) and $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{N_3C_2(H)(CO_2Me)\}(Cp)_2]$ (M = Fe, R= Me, **7a**; M = Ru, R = Xyl, **7b**) (Scheme 5). In a similar fashion, the reaction of **5a** with fumaronitrile (NC)(H)C=C(H)(CN) under analogous conditions affords the triazolato product $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{N_3C_2(H)(CN)\}(Cp)_2]$, **8**. All these products have been obtained in good yields (70-90 %) after column chromatography and fully characterised spectroscopically *via* IR and NMR. Moreover, the molecular structures of **6b** and **8** have been determined by X-ray diffraction studies (Figures 4 and 5, and Tables 5 and 6). The formation of **6-8** proceeds *via* [3+2] cycloaddition of the alkyne or the alkene, as previously demonstrated for mononuclear azido complexes [7, 20]; in the case of **8**, the reaction is accompanied by loss of HCN.

Scheme 5

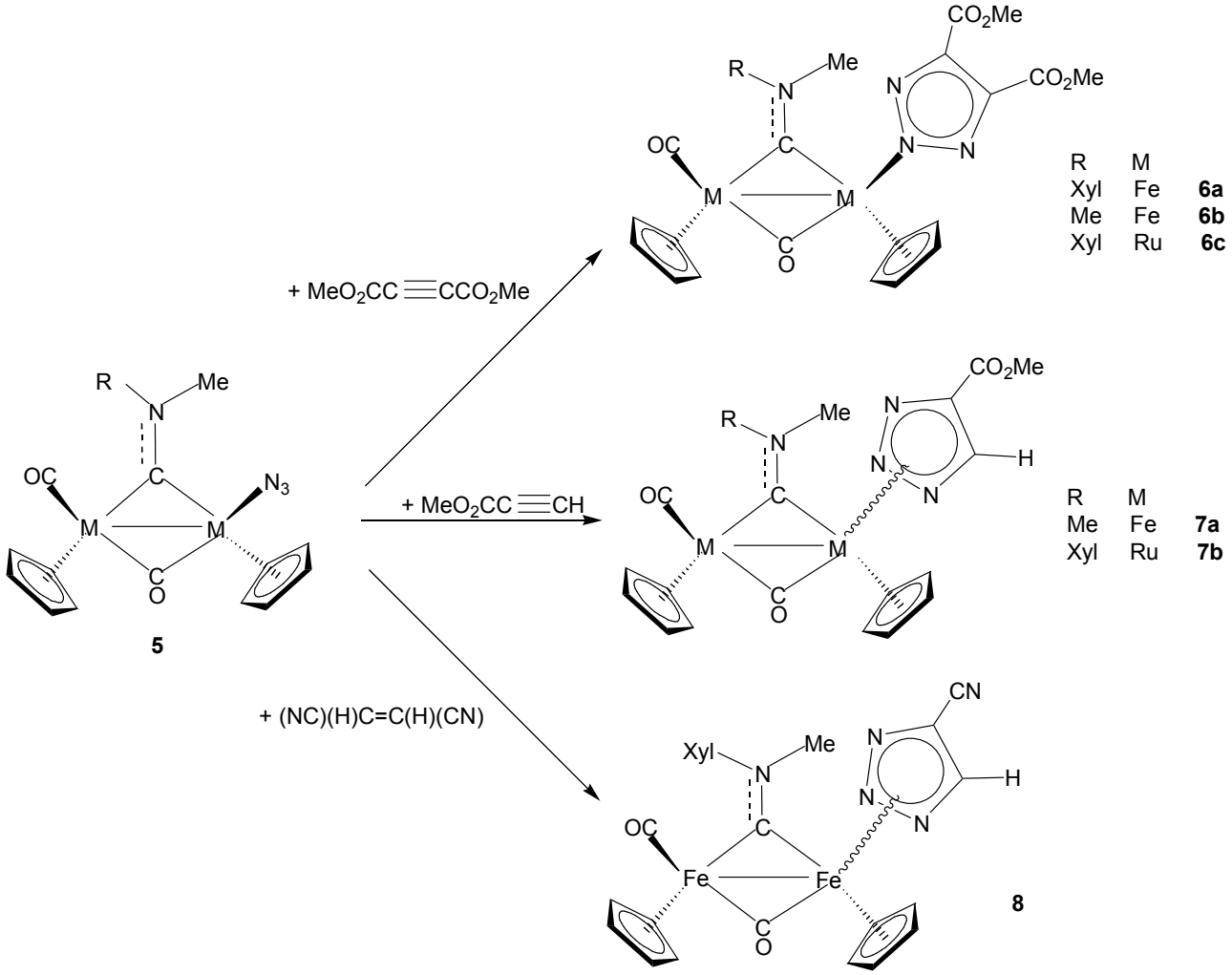

+ MeO2CC≡CCO2Me
+ MeO2CC≡CH
+ (NC)(H)C=C(H)(CN)
5
R M
Xyl Fe 6a
Me Fe 6b
Xyl Ru 6c
R M
Me Fe 7a
Xyl Ru 7b
8

Figure 4

Molecular structure of **6b**, with key atoms labelled (all H atoms have been omitted). Displacement ellipsoids are at 30% probability level. Only one of the two independent molecules is represented.

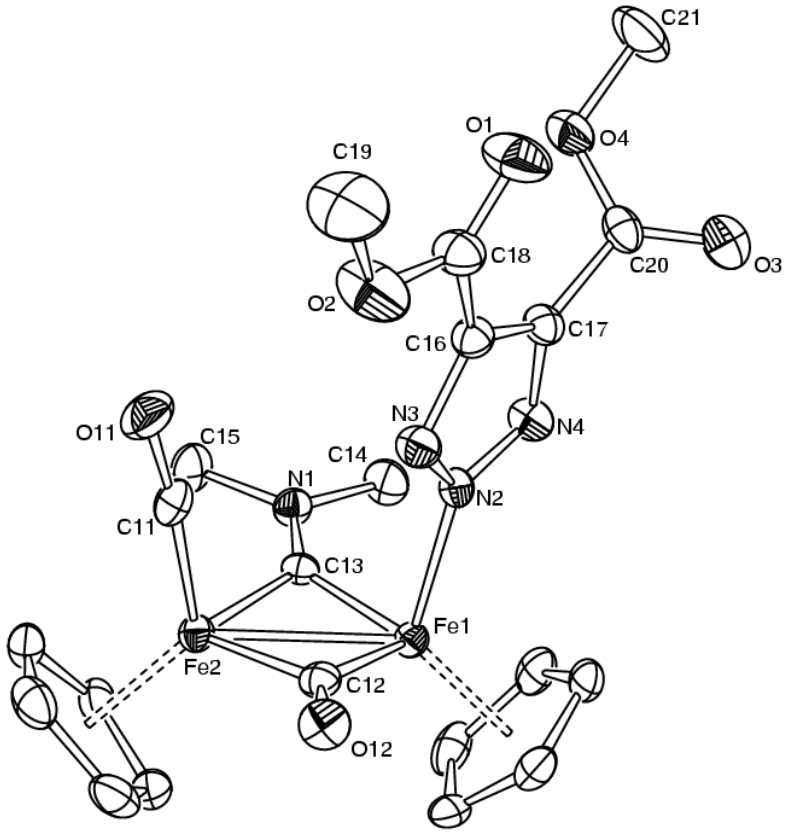


Table 5

Selected bond lengths (Å) and angles (°) for the two independent molecules of complex **6b**.

Fe(1)-Fe(2)	2.5200(11)	Fe(3)-Fe(4)	2.5062(11)
Fe(2)-C(11)	1.753(5)	Fe(4)-C(41)	1.755(6)
Fe(1)-C(12)	1.881(5)	Fe(3)-C(42)	1.861(5)
Fe(2)-C(12)	1.968(5)	Fe(4)-C(42)	1.969(5)
Fe(1)-C(13)	1.842(5)	Fe(3)-C(43)	1.845(5)
Fe(2)-C(13)	1.885(4)	Fe(4)-C(43)	1.877(5)
Fe(1)-N(2)	1.998(4)	Fe(3)-N(6)	1.989(4)
N(2)-N(3)	1.318(5)	N(6)-N(7)	1.315(5)
N(2)-N(4)	1.330(5)	N(6)-N(8)	1.320(5)
N(3)-C(16)	1.362(6)	N(7)-C(46)	1.369(6)
N(4)-C(17)	1.347(6)	N(8)-C(47)	1.354(6)

C(16)-C(17)	1.391(6)	C(46)-C(47)	1.383(6)
C(11)-O(11)	1.149(6)	C(41)-O(41)	1.141(5)
C(12)-O(12)	1.176(5)	C(42)-O(42)	1.178(5)
C(13)-N(1)	1.305(5)	C(43)-N(5)	1.307(6)
Fe(1)-C(12)-Fe(2)	81.77(19)	Fe(3)-C(42)-Fe(4)	81.7(2)
Fe(1)-C(13)-Fe(2)	85.06(19)	Fe(3)-C(43)-Fe(4)	84.6(2)
Fe(1)-N(2)-N(3)	123.0(3)	Fe(3)-N(6)-N(7)	124.8(3)
N(2)-N(3)-C(16)	105.0(4)	N(6)-N(7)-C(46)	104.9(4)
N(3)-C(16)-C(17)	107.3(4)	N(7)-C(46)-C(47)	107.3(4)
C(16)-C(17)-N(4)	108.5(4)	C(46)-C(47)-N(8)	108.3(4)
C(17)-N(4)-N(2)	104.7(4)	C(47)-N(8)-N(6)	104.8(4)

Figure 5

Molecular structure of **8**, with key atoms labelled (all H atoms, except H23, have been omitted). Displacement ellipsoids are at 30% probability level.

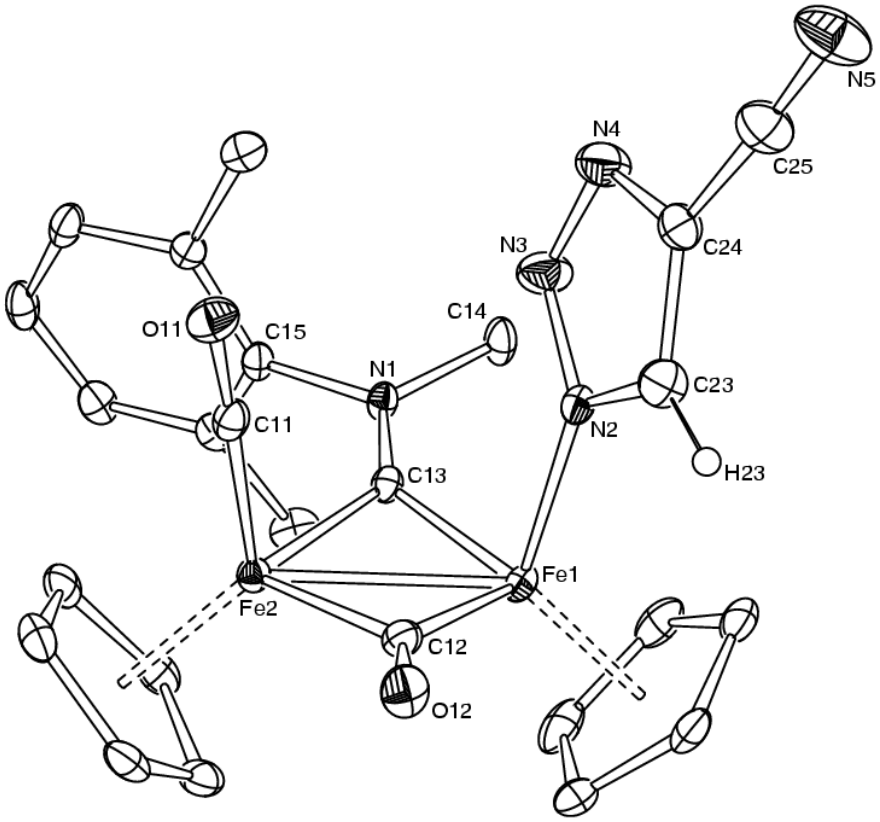


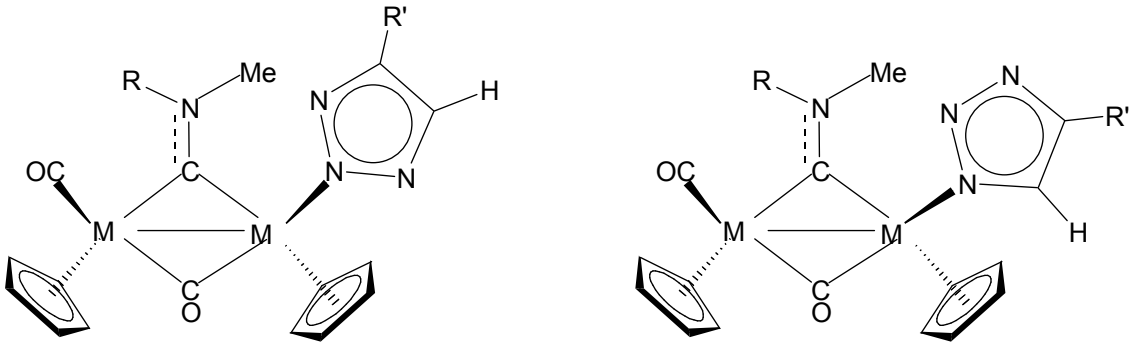
Table 6

Selected bond lengths (Å) and angles (°) for complex **8**.

Fe(1)-Fe(2)	2.5084(8)		
Fe(2)-C(11)	1.760(3)	N(2)-N(3)	1.351(2)
Fe(1)-C(12)	1.880(3)	N(3)-N(4)	1.326(4)
Fe(2)-C(12)	1.977(3)	N(4)-C(24)	1.336(4)
Fe(1)-C(13)	1.863(2)	C(23)-C(24)	1.377(4)
Fe(2)-C(13)	1.892(2)	C(24)-C(25)	1.432(4)
Fe(1)-N(2)	1.970(2)	C(25)-N(5)	1.151(4)
C(11)-O(11)	1.150(3)	C(13)-N(1)	1.305(3)
C(12)-O(12)	1.179(3)	C(14)-N(1)	1.481(3)
Fe(1)-C(12)-Fe(2)	81.10(10)	N(3)-N(4)-C(24)	107.1(2)
Fe(1)-C(13)-Fe(2)	83.83(10)	N(4)-C(24)-C(23)	108.8(2)
Fe(1)-N(2)-N(3)	122.66(18)	C(24)-C(23)-N(2)	106.7(2)
N(2)-N(3)-N(4)	110.0(2)	C(24)-C(25)-N(5)	176.9(4)

The asymmetric unit of **6b** contains two independent molecules, with similar relative arrangement of the atoms, similar bond lengths and bond angles but opposite absolute structure. The molecular structures of **6b** and **8** exhibit a *cis* arrangement of the Cp ligands; moreover, in the case of **8** where the bridging aminocarbyne ligand is asymmetrically substituted, the bulkier Xyl group points in the direction of the terminal CO ligand. The triazolato ligand is N(2) coordinated in **6b**, whereas it is bound to iron *via* N(1) in **8**. Both these coordination modes of the triazolato ligand have been previously reported [20a]; molecular orbital calculations [21] indicate that these two bonding modes are essentially isoenergetic. Evidence obtained to date indicates that either two isomers N(1) and N(2) are formed simultaneously or only the N(2) isomer is produced exclusively [7, 20c, 22]. Our work completely support this hypothesis; in fact, in the case of complexes **6** which contain a symmetrically disubstituted triazolato ligand $N_3C_2(CO_2Me)_2$, only the N(2)-bound isomer is formed as shown by NMR data. Conversely, the complexes **7-8,** which posses a monosubstituted triazolato ligand, are formed as a mixture of N(1) and N(2) isomers (Scheme 6).

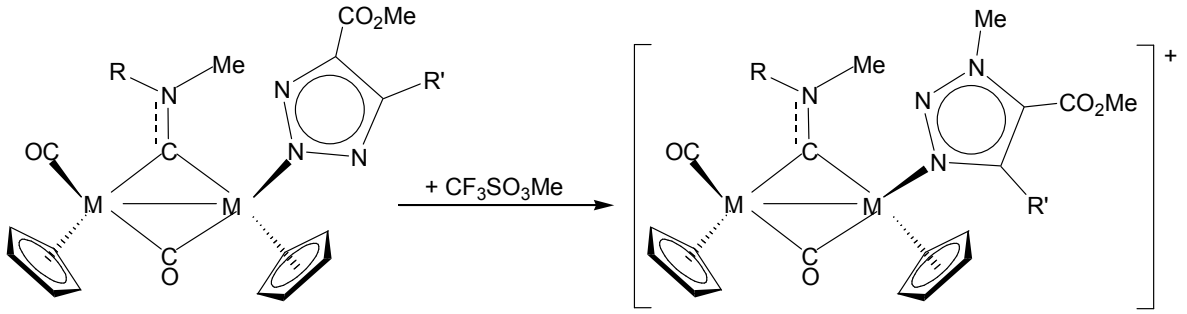
Scheme 6



The IR spectra for **6-8** show two ν(CO) at frequencies similar to the starting azido complexes **5**, indicating a similar electronic character of the two ligands. As a consequence of the symmetrical N(2) coordination, the carbon atoms of the triazolato ligand and the two COOMe substituents in **6** are equivalent and give rise to single NMR resonances [*e.g.* δ_H 3.7-3.8 ppm for $CO_2\mathit{Me}$; δ_C *ca*. 162, 140 and 52 ppm for $N_3C_2(\mathit{C}O_2Me)_2$, $N_3\mathit{C}_2(CO_2Me)_2$ and $N_3C_2(CO_2\mathit{Me})_2$, respectively]. Conversely, for **7-8** two sets of resonances are present for the N(2) and N(1) isomers [N(2) : N(1) isomer ratio = 1.1-2 : 1]. NOE studies clearly indicate that the major isomer is the N(1)-bound, which is the one also present in the solid state for **8**. For instance, irradiation of the triazolato proton (δ_H 7.74 ppm) in the major isomer of **8** produces a strong enhancement of the resonance of one Cp ligand, whereas no effect is observed after irradiation of the corresponding resonance in the minor isomer (δ_H 7.46 ppm).

The triazolato complexes **6-7** react in CH_2Cl_2 solution with CF_3SO_3Me affording the N-methylated cationic complexes $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{N_3(Me)C_2(CO_2Me)_2\}(Cp)_2][CF_3SO_3]$, **9**, and $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{N_3(Me)C_2(H)(CO_2Me)\}(Cp)_2][CF_3SO_3]$ (M = Fe, R = Me, **10a**; M = Ru, R = Xyl, **10b**), in good yields (90-95 %) (Scheme 7).

Scheme 7

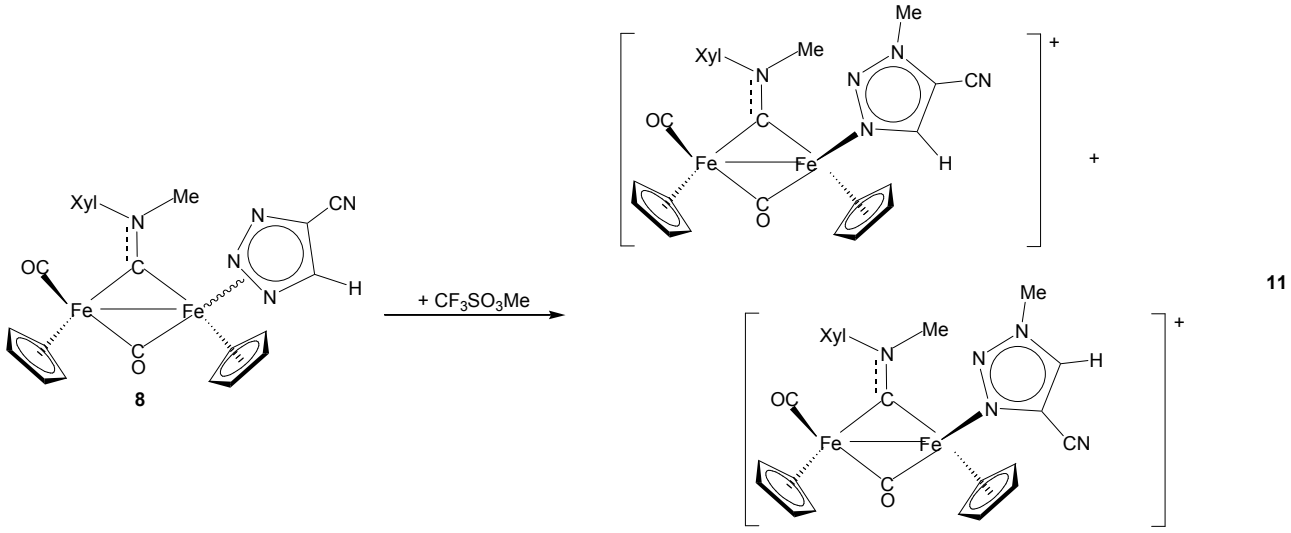


R	R'	M	
Xyl	CO_2Me	Fe	**6a**
Me	H	Fe	**7a**
Xyl	H	Ru	**7b**

R	R'	M	
Xyl	CO_2Me	Fe	**9**
Me	H	Fe	**10a**
Xyl	H	Ru	**10b**

Their NMR spectra show the presence in solution of a single species; NOE experiments on **10b** clearly indicate a strong interaction between one Cp ligand and the CH proton of the triazole ring, suggesting that methylation occurs selectively at N(3) and the triazole is N(1) coordinated. It is interesting to notice that in previous works [7] a similar regiochemistry for the methylation process was observed, but it was, then, followed by the release of the triazole molecule. Conversely, in our case the complexes **9-10** are stable in solution and do not lose the heterocycle ligand. In a similar way, the methylation of **8** results in the nearly quantitative formation of the complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{N_3(Me)C_2(H)(CN)\}(Cp)_2][CF_3SO_3]$, **11**. The IR spectrum shows the usual ν(CO) for the terminal and bridging carbonyls at frequencies similar to those observed for **9-10**, and ν(CN) at 2220 cm^{-1}; hence, also in this case methylation has occurred on the triazolato ring. The NMR spectra show the presence of two isomers in a 1.2:1 ratio and with very similar but distinct resonances. This can be explained assuming that the methylation of **8** is not regioselective, but it can occur on both N(1) and N(3) (Scheme 8).

Scheme 8



4. Conclusions

This study shows that dimetallic aminocarbyne complexes containing pseudohalide ligands can be obtained by MeCN displacement from $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(MeCN)(Cp)_2][SO_3CF_3]$ (M = Fe, R= Xyl, **1a**; M = Fe, Me, **1b**; M = Ru, R = Xyl, **1c**; M = Ru, R = Me, **1d**). We had previously shown that nitrile substitution in **1** could be used also for the introduction of other N-donor ligands, such as amines and imines [18]. All these reactions are completely selective, and no product of addition of the N-nucleophile has been observed during our work, even though nucleophilic additions to coordinated nitriles have been widely documented in the literature [23]. Probably, the MeCN ligand in **1** is not sufficiently activated to react with N-nucleophiles, whereas it reacts easily with C-nucleophiles [9a, 9c, 10c].

The results reported in this paper suggest that nitrile substitution in **1** proceeds with inversion of the configuration of the metal-centre and, in fact, the products obtained at room temperature present a *trans* geometry of the Cp ligands, whereas the parent complexes **1** have a *cis* structure. Moreover, *trans* to *cis* isomerisation occurs at high temperature, indicating that the *trans* isomer is the kinetic product whereas the *cis* species is the thermodynamic one, as previously found for the vinyliminium complexes $[Fe_2\{\mu\text{-}\sigma\text{:}\eta^3\text{-}C(R')=C(R'')C=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ [10a, 10b].

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 253688 for *trans*-**2b**, 253689 for **4b**·CH_2Cl_2, 253690 for **5a**, 253691 for **6b**·**0.5**CH_2Cl_2 and 253692 for **8**·CH_2Cl_2**.** Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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Graphical abstract

Diiron and diruthenium aminocarbyne complexes containing pseudohalide ligands (*i.e.* NCS^-, NCO^-, N_3^-) have been obtained by nitrile replacement; both *cis* and *trans* isomers can be formed depending on the reaction temperature and *trans* to *cis* isomerisation is observed at high temperature. The terminal azido ligand undergoes 1,3-dipolar cycloaddition reactions with alkynes and fumaronitrile, affording new dinuclear triazolato complexes.