

Oxidative Dimerization of Triarylamines Promoted by WCl_6 , Including the Solid State Isolation and the Crystallographic Characterization of a Triphenylammonium Salt

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Abstract

The triphenylammonium salt $[\text{NHPH}_3][\text{WCl}_6]$, **1**, and the product of the C–C dimerization of triphenylamine, $\text{Ph}_2\text{N}(\text{C}_6\text{H}_4)_2\text{NPh}_2$, **2**, were afforded from the reaction between WCl_6 and NPh_3 in CH_2Cl_2 . Compound **2** was isolated in 43% yield upon hydrolysis of the reaction mixture. The X-ray structure of **1** provides the first crystallographic characterization of the triphenylammonium ion. Combined EPR and DFT studies gave insight into the reaction mechanism, and allowed the identification of $\text{WCl}_5 \cdots [\text{Cl}(\text{C}_6\text{H}_4)\text{NPh}_2]$ as a presumable key intermediate. The reactions of WCl_6 with 4-bromotriphenylamine, 4,4'-dimethyltriphenylamine, 9-phenylcarbazole, followed by hydrolytic treatment, led to the dimerization products **3-6**, in admixture with variable amounts of the parent amines. *N,N,N',N'*-tetrakis(4-bromophenyl)-[1,1'-biphenyl]-4,4'-diamine, **3**, was isolated in 60% yield from the reaction of WCl_6 with 4,4'-dibromotriphenylamine.

Keywords: coordination chemistry, tungsten hexachloride, triaryl amines, triphenylammonium, C–H activation, C–C coupling

Introduction

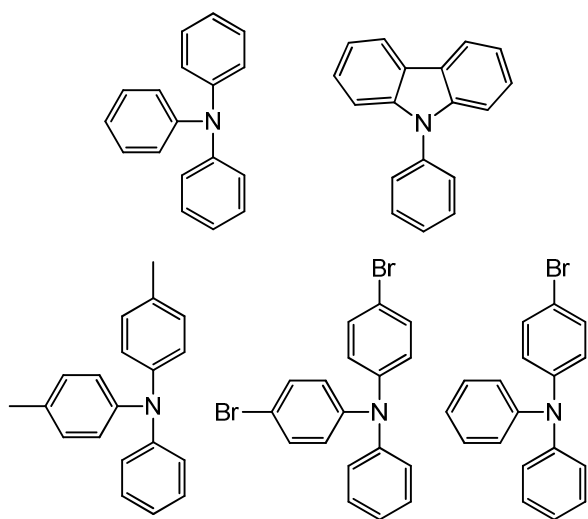
The coordination of amines to low valent transition metal centers represents a cornerstone of inorganic chemistry, and, relevantly, a large variety of amine containing metal complexes have been reported to exhibit useful properties.¹ Activation of the amine ligand has been observed within a number of low valent metal halides, usually occurring via well defined reaction pathways.²

The chemistry of amines with high valent, groups 4-6 metal halides is a more complicated issue. This type of complexes usually manifest their strongly acidic nature upon reaction with primary and secondary aliphatic amines, yielding mixtures of aminolysis products.³ Also aliphatic tertiary amines

may be activated by high valent groups 4-6 metal chlorides,⁴ and especially the TiCl_4 /trialkylamine system works as an interesting catalyst for organic synthesis.⁵ In general, these reactions seem to proceed with *amine to metal* electron transfer followed by amine C–H bond cleavage, however the mechanistic details have been largely not understood. In this respect, we have recently elucidated the interaction of WCl_6 with tribenzylamine, leading to the straightforward formation of W(V) salts of the relevant ammonium and iminium cations, respectively.⁶

Information on the reactivity of triarylamines with high valent metal halides are almost absent in the literature;⁷ to the best of our knowledge, the only coordination compounds were claimed to be prepared by addition of variable amounts of NPh_3 to NbCl_5 in low polar solvents.⁸

In the framework of our interest in the chemistry of WCl_6 ,^{6,9} herein we report a study on the reactions with triphenylamine, a selection of its substituted derivatives and N-phenylcarbazole (Scheme 1). In particular, a possible mechanism for the reaction between WCl_6 and NPh_3 is proposed, on the basis of spectroscopic and DFT outcomes.



Scheme 1. Triarylamines treated in the present work.

Results and discussion

The reaction of WCl_6 with a slight excess of triphenylamine (NPh_3)¹⁰ was carried out in dichloromethane^{7a} at room temperature and afforded a red-brown mixture. The W(V) salt $[\text{NHPH}_3][\text{WCl}_6]$, **1**, was isolated in 40% yield by a crystallization procedure. Magnetic analysis on **1** ($\mu_{\text{eff}} = 0.99$ BM) was consistent with previous findings regarding $[\text{WCl}_6]^-$ salts.^{6,9,11} Evidence for the presence of the NH proton in **1** was supplied by ^1H NMR spectroscopy (CD_2Cl_2 solution), showing a broad resonance at 10.8 ppm. A weak absorption at 2947 cm^{-1} in the IR spectrum (solid state) was attributed to the N–H stretching vibration by comparison with the corresponding calculated IR spectrum (*vide infra*). Due to its low basicity, NPh_3 rarely forms salts,¹² and the only well defined triphenylammonium salts were previously prepared by combination of NPh_3 with superacids.^{12a}

The molecular structure of **1** was ascertained by X-ray diffractometry: a view of the structure is shown in Figure 1, while relevant bonding parameters are reported in Table 1.

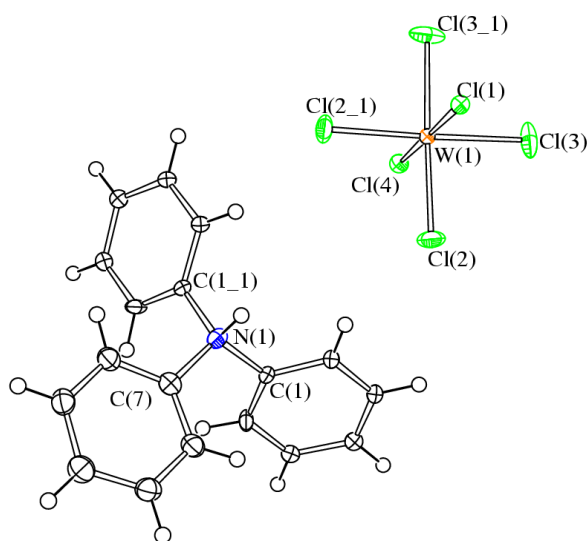


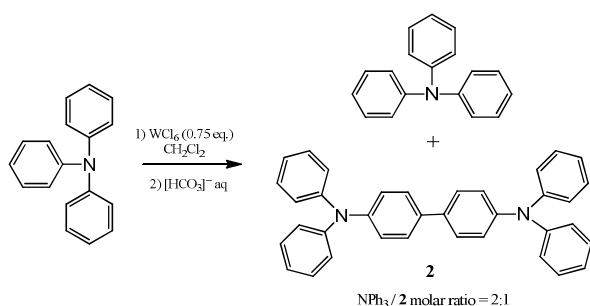
Figure 1. Molecular structure of $[\text{NHPH}_3][\text{WCl}_6]$, **1**. Displacement ellipsoids are at the 50% probability level. Symmetry transformation used to generate equivalent atoms: $x, -y+3/2, z$.

Table 1. Selected bond distances (Å) and angles (°) for **1**. Symmetry transformations used to generate equivalent atoms: $x, -y+3/2, z$.

W(1)–Cl(1)	2.310(3)	W(1)–Cl(2)	2.313(2)
W(1)–Cl(3)	2.342(2)	W(1)–Cl(4)	2.339(3)
N(1)–C(1)	1.518(10)	N(1)–C(7)	1.522(16)
Cl(1)–W(1)–Cl(4)	178.13(12)	Cl(2)–W(1)–Cl(3 ₁)	177.46(10)
Cl(3)–W(1)–Cl(2 ₁)	177.46(10)	C(1)–N(1)–C(7)	113.0(6)

The solid state structure of **1** consists of octahedral $[\text{WCl}_6]^-$ anions and $[\text{NHPh}_3]^+$ cations. The bonding parameters of $[\text{WCl}_6]^-$ resemble previous findings for the same anion in miscellaneous salts.^{6,9,13} For what concerns the $[\text{NHPh}_3]^+$ cation, its structure has not been described heretofore. The N–C bonds in this cation [1.518(10)–1.522(16) Å] are significantly elongated compared to the neutral amine NPh_3 [1.42–1.43 Å], as a consequence of the protonation of the nitrogen atom. The N(1)–H(1) group of the $[\text{NHPh}_3]^+$ cation behaves as H-donor towards the chloride atoms of two adjacent anions [N(1)–H(1) 0.89(2) Å; H(1)⋯Cl(3_2) 2.89(5) Å; H(1)⋯Cl(3_3) 2.89(5) Å; N(1)⋯Cl(3_2) 3.590(9) Å; N(1)⋯Cl(3_3) 3.590(9) Å; $\angle\text{N(1)H(1)Cl(3_2)}$ 136(6)°; $\angle\text{N(1)H(1)Cl(3_1)}$ 136(6)°; symmetry transformations used to generate equivalent atoms: $_2 x+1/2, -y+3/2, -z+1/2, _3 x+1/2, y, -z+1/2$].

In order to understand the source of the proton as found in **1**, we treated the solid residue obtained from $\text{WCl}_6/\text{NPh}_3$ in CH_2Cl_2 with an aqueous $[\text{HCO}_3]^-$ solution. Indeed hydrolysis is an effective method for separating organic compounds from WCl_6 -derived metal species.^{9c,d} After removal of the volatiles, triphenylamine (NPh_3) and *N,N,N',N'*-tetraphenyl-biphenyl-4,4'-diamine, **2**, were detected in ca. 2:1 molar ratio via NMR spectroscopy. Then **2** was isolated in 43% yield by chromatographic purification (Scheme 2).



Scheme 2. Organic products of the reaction between NPh_3 and WCl_6 , isolated after hydrolysis.

The outcome depicted in Scheme 2 suggests that the formation of **2** takes place with protonation of part of the amine reactant, to afford the ammonium salt **1**. Accordingly, a NMR experiment has pointed that the solvent is not involved in this protonation (see Experimental, NMR studies), while the hypothetical formation of H₂ was ruled out by GC analysis of the reaction atmosphere.

A joint EPR and DFT study on the WCl₆/NPh₃ system led to outline a plausible reaction pathway, which is represented in Figure 2; in agreement with the proposed pathway, the overall reaction is written in compact form in Eqn. 1.¹⁰

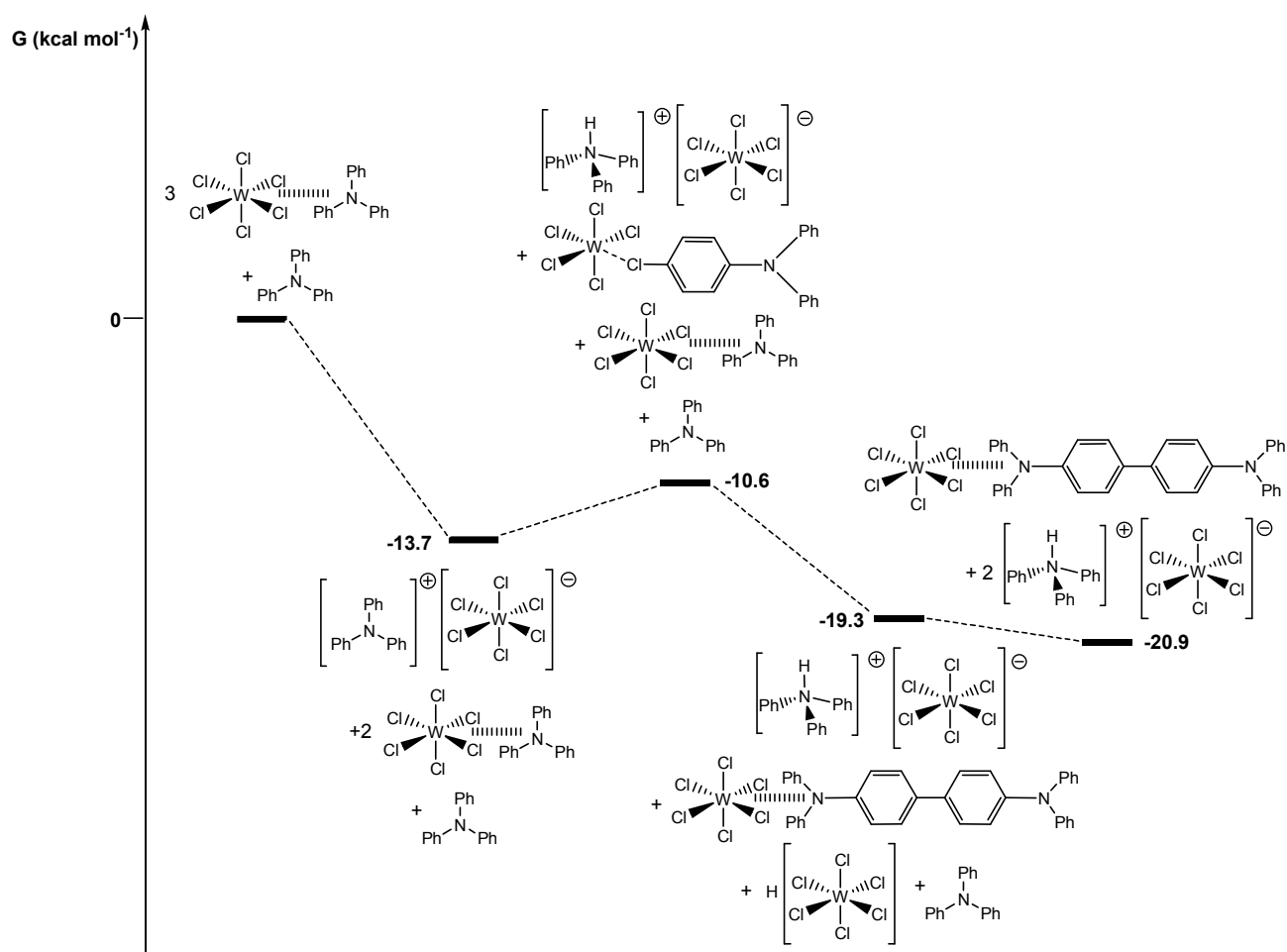
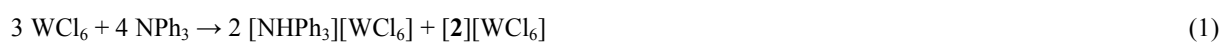


Figure 2. Calculated relative Gibbs free energies (CPCM/M06) of the species involved in the reaction between WCl_6 and NPh_3 in CH_2Cl_2 .

The optimized structure of **1** (M06 functional) was calculated considering dichloromethane as implicit solvent (see Figure S1 and Table S1 within the SI). In general, the calculated bonding parameters of **1** are in quite good agreement with the corresponding X-ray data (Table S1). However, in the computed structure, the H---Cl hydrogen bond interaction leads to elongations of the corresponding N–H and W–Cl bonds, that are not observed in the solid state X-Ray structure. The different mutual orientation of the cation and the anion in the DFT-optimized geometry with respect to the experimental one, attributable to the introduction of a solvation model and to the lack of packing forces, does not allow a direct comparison of W–Cl bonding parameters.

The same computational approach was adopted for all the other species possibly involved in the reaction. The initial interaction between WCl_6 and NPh_3 is expected to generate the transient adduct $\text{WCl}_6 \cdots \text{NPh}_3$ (Figure S2, Table S2),¹⁴ followed by mono-electron transfer to give the radical cation salt $[\text{NPh}_3][\text{WCl}_6]$ (Figure S3, Table S3).¹⁵ A reaction solution was analyzed by NMR and EPR spectroscopy after 20-60 minutes. The ^1H NMR spectrum showed very broad resonances at 29.7 ppm and in the range 7.5-3.9 ppm, in accordance with the presence of paramagnetic organic species. The EPR spectrum is the result of the superimposition of the spectra related to five radical compounds, whose identities were assigned on the basis of computer simulations (Figure 3 and Figure S4). More precisely, $[\text{NPh}_3]^+$ was recognized in low amount,¹⁶ while $[\text{WCl}_6]^-$ was not observed, in analogy with previous EPR investigations on analogous systems.⁶ Traces of W(V) oxido complexes, tentatively identified as $\text{WOCl}_3(\text{NPh}_3)_2$ ($g_0 = 1.91195$) and $\text{WOCl}_3(\text{NPh}_3)$ ($g_0 = 1.88282$), were recognized, presumably as consequence of adventitious hydrolysis. The major species detected by EPR in solution is likely to be the adduct $\text{WCl}_5 \cdots [\text{Cl}(\text{C}_6\text{H}_4)\text{NPh}_2]$ (Figure S5, Table S4). The formation of (4-chlorophenyl)-di(phenyl)amine from triphenylamine was previously achieved by a non selective

reaction using thionyl chloride as a chlorinating agent.¹⁷ A view of the calculated structure of $WCl_5 \cdots [Cl(C_6H_4)NPh_2]$, including the spin density surface, is shown in Figure 4. This structure exhibits a covalent C-Cl bond (bond length 1.762 Å, Mayer bond order 0.98). On the other hand, the $W \cdots Cl(C_6H_4)NPh_2$ bond order is quite low (0.34) compared to the remaining W-Cl bonds (average bond order 1.24). Hydrogen transfer from $[NPh_3][WCl_6]$ to $WCl_6 \cdots NPh_3$ would give reason for the formation of both $WCl_5 \cdots [Cl(C_6H_4)NPh_2]$ and **1**.

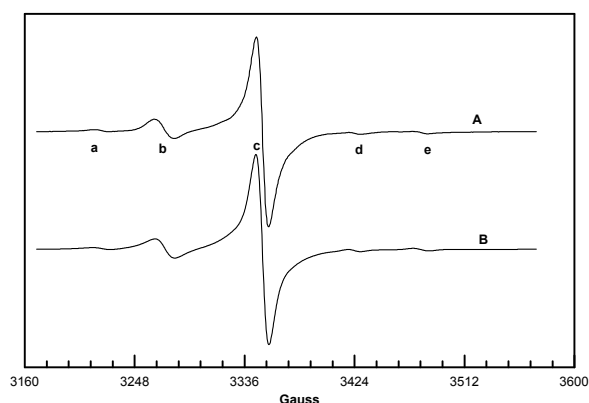


Figure 3. View of the EPR spectrum of the mixture obtained from WCl_6/NPh_3 (3:4 ratio) in CH_2Cl_2 after 1 hour (A experimental, B calculated).

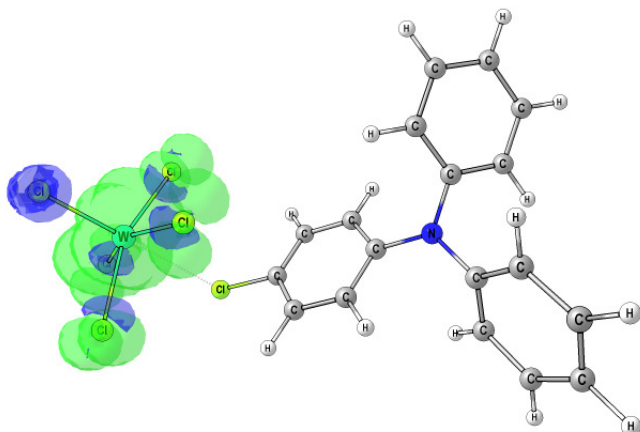
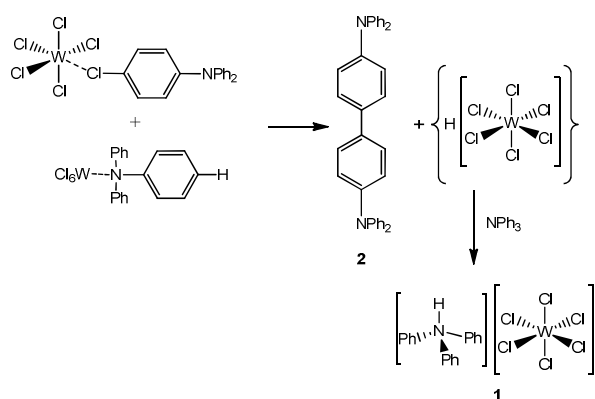


Figure 4. Calculated structure of $WCl_5 \cdots [Cl(C_6H_4)NPh_2]$ (C-PCM/M06, dichloromethane as implicit solvent), and related spin density surface (surface isovalue = 0.001 a.u.).

The C–C coupling step might be viewed as the electrophilic attack of an aminobenzene ring to an activated haloarene, affording **2** and H[WCl₆] (Scheme 3). This resembles a series of non catalyzed reactions affording substituted biphenyls, which were previously reported.¹⁸ The presumably highly reactive H[WCl₆] might contribute to yield **1** by combination with NPh₃.



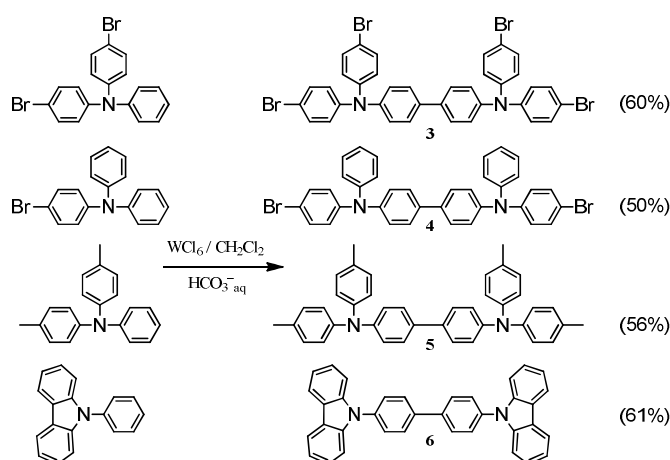
Scheme 3. Formation of **1** and **2**.

[**2**]⁺ was found (EPR) to be the only radical species in the reaction solution after 48 hours (Figure S6), thus suggesting that **2**, once formed, is able in its turn to give mono-electron transfer to tungsten (Eqn. 1).^{16,19}

C–C coupling reactions between conjugated systems, generally promoted by oxidative conditions and proceeding with C–H bond activation, represent a well known category of organic transformations.²⁰ In particular, the C–C dimerization products of triaryl amines have been commonly accessed by the so called Ullmann condensation reaction, in the presence of a suitable catalyst.^{21,23} However, also approaches based on amine oxidation have been considered, and an efficient metal-based system has been proposed by Gopidas and coworkers, making use of copper(II) perchlorate.²²

Triphenylamine, its dimerization product (*N,N,N',N'*-tetraphenylbenzidine) and the respective substituted derivatives have aroused interest as possible hole-transport materials in optoelectronic devices²³ and porous organic frameworks for gas uptake.²⁴

We performed the reactions of WCl_6 with a series of substituted triphenylamines in order to see whether the behavior of the WCl_6/NPh_3 system held general character or not. The reactions were conducted in dichloromethane by using a $W/amine = 0.75$ ratio, in accordance with Eqn. 1. The final reaction mixtures were treated with basic aqueous solution in order to separate the organic products from the inorganic substrate. Thus, the reaction of WCl_6 with 4,4'-dibromotriphenylamine led, after work up, to the isolation of *N,N,N',N'*-tetrakis(4-bromophenyl)-[1,1'-biphenyl]-4,4'-diamine, **3**, in 60% yield (Scheme 4). Compound **3** was characterized by elemental analysis and NMR spectroscopy. Even the dimerization products *N,N'*-diphenyl-*N,N'*-bis(4-bromophenyl)-[1,1'-biphenyl]-4,4'-diamine, **4**, *N,N,N',N'*-tetrakis(4-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine, **5**, and 4,4'-dicarbazole-1,1'-biphenyl, **6**, were found in the reaction mixtures as generated from the respective triaryl amines (Scheme 4). Compounds **4-6** were quantified by NMR spectroscopy, and all the attempts to separate them from the parent amines failed.



Scheme 4. WCl_6 -promoted formation of dimerization products of substituted triphenylamines (yield given respect to the starting amine).

Conclusions

The chemistry of high valent transition metal halides with tertiary amines has been limitedly elucidated so far. Herein, we have described a rare example of well defined interaction of a high valent metal halide (WCl_6) with a triarylamine (NPh_3). Alternatively to the behavior exhibited by WCl_6 towards

other nitrogen donors,²⁵ here the oxidative power of the W(VI) centre promotes intermolecular hydrogen migration via Csp^2 -H bond activation and, then, dimerization of part of the amine substrate. The hydrogen migration unusually generates, as a co-product, a triphenylammonium salt, which has been crystallographically characterized. The dimerization process has been observed also with a series of substituted triphenylamines.

Experimental

The reaction vessels were oven dried at 140°C prior to use, evacuated (10^{-2} mmHg) and then filled with argon. WCl_6 (99.9%, Strem), amines (TCI Europe) and deuterated solvents (98+%, Cortecnet) were commercial products stored under argon atmosphere as received. Silica (Silica gel 60, 7-230 mesh) and alumina (Brockmann grade III) for chromatographic separations were purchased from Sigma Aldrich. When isolated, the metal products were conserved in sealed glass tubes under argon. Solvents (Sigma Aldrich) were distilled from appropriate drying agents under argon atmosphere before use. Infrared spectra were recorded at 298 K on a FT IR-Perkin Elmer Spectrometer, equipped with UATR sampling accessory. Magnetic susceptibility (reported per W atom) was measured at 298 K on solid sample with a Magway MSB Mk1 magnetic susceptibility balance (Sherwood Scientific Ltd.). Diamagnetic corrections were introduced according to König.²⁶ NMR spectra were recorded on a Bruker Avance II DRX400 instrument equipped with BBFO broadband probe at 298 K. The chemical shifts for 1H and ^{13}C were referenced to the non-deuterated aliquot of the solvent. EPR spectra were recorded at 298 K on a Varian (Palo Alto, CA, USA) E112 spectrometer operating at X band, equipped with a Varian E257 temperature control unit and interfaced to IPC 610/P566C industrial grade Advantech computer, using acquisition board ²⁷ and software package especially designed for EPR experiments.²⁸ Experimental EPR spectra were simulated by the WINSIM 32 program.²⁹ Carbon, hydrogen and

nitrogen analyses were performed on Carlo Erba mod. 1106 instrument. The chloride content was determined by the Mohr method³⁰ on solutions prepared by dissolution of the solid in aqueous KOH at boiling temperature, followed by cooling to room temperature and addition of HNO₃ up to neutralization.

Reaction of WCl₆ with NPh₃.

A) Synthesis and isolation of [NHPPh₃][WCl₆], **1.** A solution of NPh₃ (0.240 g, 0.978 mmol) in CH₂Cl₂ (20 mL) was treated with WCl₆ (0.380 g, 0.957 mmol). A bright-green solution was observed after 5-20 minutes. The mixture was stirred for additional 24 h. The final red solution was filtered in order to remove some dark-brown solid, then it was concentrated to *ca.* 10 mL, layered with hexane and set aside at -30 °C. Compound **1** was recovered as a dark-red crystalline solid after some days. Yield: 0.246 g, 40%. Anal. Calcd for C₁₈H₁₆Cl₆NW: C, 33.63; H, 2.51; N, 2.18; Cl, 33.09. Found: C, 33.75; H, 2.67; N, 2.03; Cl, 33.20. IR (solid state): 3050w, 3004w, 2947w ($\nu_{\text{N-H}}$), 1606m, 1575vs, 1474vs, 1452m-sh, 1355vs, 1326m-sh, 1305m, 1273s, 1251m, 1187m, 1177s, 1073w-m, 1022w, 998m, 979s, 896w, 838w, 819m, 753m, 708m, 688vs cm⁻¹. Magnetic measurement: $\chi_{\text{M}}^{\text{corr}} = 4.10 \times 10^{-4}$ cgsu, $\mu_{\text{eff}} = 0.99$ BM. ¹H NMR (CD₂Cl₂): $\delta = 10.84$ (br, 1 H, NH); 7.69, 7.45 (br, 15 H, Ph) ppm. ¹³C{¹H} NMR (CD₂Cl₂): $\delta = 139.8$ (*ipso*-Ph); 131.9, 131.3, 126.8 (Ph) ppm.

B) NMR studies. WCl₆ (0.160 g, 0.403 mmol), CD₂Cl₂ (0.70 mL) and NPh₃ (0.098 g, 0.399 mmol) were introduced into a NMR tube in the order given. The tube was sealed and shaken in order to homogenize the content. Subsequent NMR spectra were recorded at 20°C. 1) After 20 minutes (green solution), ¹H NMR (CD₂Cl₂): $\delta = 29.7, 7.5-3.9$ (br) ppm. 2) After 48 h, the solution turned red-brown; ¹H NMR analysis evidenced the presence of **1** and broad resonances which could not be assigned.

C) EPR studies. The sample for EPR analyses was prepared as follows. A mixture of WCl₆ (0.150 mmol) and NPh₃ (0.150 mmol) in CH₂Cl₂ (15 mL) was allowed to stir at 10 °C for 5 minutes, in a

Schlenk tube. Then an aliquot of the resulting green solution was diluted with CH₂Cl₂ (*ca.* 1:10) and transferred into an EPR tube. The tube was sealed, then the EPR spectrum was recorded after 1 hour. The solution contained in the Schlenk tube was allowed to warm to room temperature and stirred for additional 48 h. Hence an aliquot of the resulting dark-red solution was introduced into an EPR tube prior dilution with CH₂Cl₂ (*ca.* 1:10). The tube was sealed before EPR analysis.

D) Synthesis and isolation of *N,N,N',N'*-tetraphenyl-[1,1'-biphenyl]-4,4'-diamine, **2.** A solution of NPh₃ (313 mg, 1.28 mmol) in CH₂Cl₂ (20 mL) was treated with WCl₆ (380 mg, 0.957 mmol). The mixture was stirred for 48 h at room temperature. The solvent was eliminated, then the residue was treated with a 0.2 M aqueous solution of KHCO₃ (30 mL). The mixture was stirred in contact with air with 18 h, hence the volatile materials were removed in vacuo. The residue was treated with CHCl₃ (30 mL), and the extracted solution was filtered on a short alumina column. The filtered solution was dried in vacuo, then the resulting residue was charged on a silica column. The use of a toluene/pentane mixture (progressively increasing ratio) as eluent allowed to recover NPh₃ (yield 126 mg, 40%). The fraction corresponding to **2** was collected by using Et₂O/toluene (progressively increasing ratio) as eluent, then **2** was isolated as a colorless solid.

2 (yield: 134 mg, 43%). Anal. Calcd for C₃₆H₂₈N₂: C, 88.49; H, 5.78; N, 5.73. Found: C, 88.26; H, 5.84; N, 5.77. ¹H NMR (CDCl₃): δ = 7.45 (d, 4H, ³J_{HH} = 8.6 Hz), 7.31-7.22 (m, 8H), 7.18-7.12 (m, 12H), 7.03 ppm (t, 4H, ³J_{HH} = 7.3 Hz). ¹³C{¹H} NMR (CDCl₃): δ = 148.2, 147.2, 135.2, 129.7, 127.7, 124.8, 124.5, 123.3 ppm.

Reaction of WCl₆ with 4,4'-dibromotriphenylamine. Synthesis and isolation of *N,N,N',N'*-tetrakis(4-bromophenyl)-[1,1'-biphenyl]-4,4'-diamine, **3.**³¹ Compound **3** was obtained by using a procedure analogous to that described for the reaction WCl₆/NPh₃, by allowing WCl₆ (411 mg, 1.04

mmol) to react with 4,4'-dibromotriphenylamine (560 mg, 1.39 mmol). A 95:5 mixture of hexane and ethyl acetate was used as eluent for silica chromatography.

3 (yield: 335 mg, 60%). Anal. Calcd for C₃₆H₂₄Br₄N₂: C, 53.77; H, 3.01; N, 3.48. Found: C, 53.89; H, 2.91; N, 3.54. ¹H NMR (CDCl₃): δ = 7.49 (d, 4H, ³J_{HH} = 8.6 Hz), 7.40 (d, 8H, ³J_{HH} = 9.06 Hz), 7.14 (d, 4H, ³J_{HH} = 8.11 Hz), 7.02 ppm (d, 8H, ³J_{HH} = 8.58 Hz). ¹³C{¹H} NMR (CDCl₃): δ = 146.4, 146.0, 135.5, 132.5, 127.7, 125.7, 124.6, 115.8 ppm.

Reactions of WCl₆ with 4-bromotriphenylamine, 4,4'-dimethyltriphenylamine, 9-phenylcarbazole. Formation and NMR identification of *N,N'*-diphenyl-*N,N'*-bis(4-bromophenyl)-[1,1'-biphenyl]-4,4'-diamine, **4,^{23e} *N,N,N',N'*-tetrakis(4-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine, **5**,²² and 4,4'-dicarbazole-1,1'-biphenyl, **6**.^{23,32}** These reactions were carried out by using the same procedure described for WCl₆/NPh₃. The organic mixtures were passed through a silica column by using a 4:1 hexane/ethyl acetate mixture as eluent, and then analyzed by NMR spectroscopy.

From WCl₆ (360 mg, 0.908 mmol) and 4-bromotriphenylamine (393 mg, 1.21 mmol): 4-bromotriphenylamine and **4** were obtained (molar ratio 1.4). Yield 330 mg (**4**, 50%).

From WCl₆ (380 mg, 0.958 mmol) and 4,4'-dimethyltriphenylamine (350 mg, 1.28 mmol): 4,4'-dimethyltriphenylamine and **5** were obtained (molar ratio 0.9). Yield 280 mg (**5**, 56%).

From WCl₆ (380 mg, 0.958 mmol) and 9-phenylcarbazole (312 mg, 1.28 mmol): 9-phenylcarbazole and **6** were obtained (molar ratio 0.8). Yield 265 mg (**6**, 61%).

X-ray Crystallography. Crystal data and collection details for **1** are listed in Table 2. The diffraction experiment was carried out on a Bruker APEX II diffractometer equipped with a CCD detector and using Mo-K α radiation ($\lambda = 0.71073$ Å). Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).³³ The structure was solved by direct methods and

refined by full-matrix least-squares based on all data using F^2 .³⁴ All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were fixed at calculated positions and refined by a riding model, except H(1) which was located in the Fourier map and refined isotropically using the 1.2 fold U_{iso} value of the parent atom. The N(1)-H(1) distances were restrained to 0.89 Å (s.u. 0.02). The asymmetric unit of the unit cell of **1** contains half of a $[\text{Ph}_3\text{NH}]^+$ cation and half of a $[\text{WCl}_6]^-$ anion, both located on a mirror plane. Restraints were on the thermal parameters of the C-atoms (SIMU .005 \$C line in SHEXL).

Table 2. Crystal data and measurement details for **1**.

Formula	$\text{C}_{18}\text{H}_{16}\text{Cl}_6\text{NW}$
FW	642.87
T, K	100(2)
λ , Å	0.71073
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
<i>a</i> , Å	13.445(4)
<i>b</i> , Å	13.353(4)
<i>c</i> , Å	11.273(3)
β , °	90
Cell Volume, Å ³	2023.8(10)
Z	4
D_c , g·cm ⁻³	2.110
μ , mm ⁻¹	6.503
F(000)	1228
Crystal size, mm	0.18×0.16×0.12
θ limits, °	2.36–25.55
Reflections collected	7161
Independent reflections	1948 [$R_{\text{int}} = 0.1105$]
Data / restraints / parameters	1948 / 73 / 129
Goodness on fit on F^2	0.992
R_1 ($I > 2\sigma(I)$)	0.0509
wR_2 (all data)	0.1186
Largest diff. peak and hole, e Å ⁻³	2.122 / -1.939

Computational studies. The computational geometry optimization of the complexes and calculation of the electron spin density was carried out without symmetry constrains, initially using the hybrid DFT EDF2 functional³⁵ or the B3LYP (Becke, three-parameter, Lee-Yang-Parr)^{36,37} exchange-correlation functional formulated with the Becke 88 exchange functional³⁸ and the correlation functional of Lee, Yang and Parr.³⁹ These functionals were used in combination with the 6-31G(d,p) basis set on the light atoms and the ECP-based LANL2DZ based basis set on tungsten.⁴⁰ Further geometry optimization was performed using the hyper-GGA functional M06⁴¹ in combination with a polarized split-valence basis

set composed by the 6-31G(d,p) set on the light atoms and the ECP-based LANL2TZ(f) set on the metal centre.⁴² C-PCM implicit solvation model ($\epsilon = 9.08$) was added.⁴³ In all of the cases, the “unrestricted” formalism was applied to systems with unpaired electrons and the absence of meaningful spin contamination was verified by comparing the computed $\langle S^2 \rangle$ values with the theoretical ones. The stationary points were characterized by IR simulations, from which zero-point vibrational energies were obtained.⁴⁴ DFT-simulated IR data, obtained with harmonic approximation, assisted the interpretation of experimental IR spectra.

B3LYP and EDF2 calculations were performed by the parallel Linux version of the Spartan 10 software,⁴⁵ while Gaussian 09⁴⁶ was used for C-PCM/M06 optimizations.

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Notes

The authors declare no competing financial interest.

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Supporting Information Available

CCDC reference number 1428972 (1) contains the supplementary crystallographic data for the X-ray study reported in this paper. These data can be obtained free of charge at

www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk). Cartesian coordinates of the DFT-optimized compounds (CPCM/M06) are reported in a separated .xyz file.

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Table of Contents Synopsis and graphic

The reaction of WCl_6 with NPh_3 proceeds via mono-electron oxidation of the organic substrate, followed by intermolecular hydrogen migration and C–C dimerization of half of the organic material.

