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A tungsten complex containing a highly delocalized metal–ligand system

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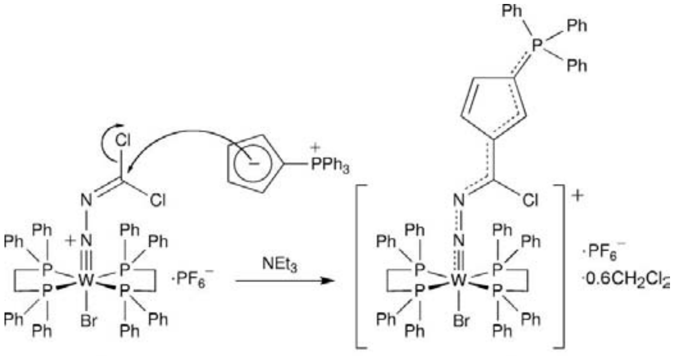
Nucleophilic attack of (triphenylphosphonio)cyclopentadienide on the dichlorodiazomethane–tungsten complex *trans*-$[BrW(dppe)_2(N_2CCl_2)]PF_6$ [dppe is 1,2-bis(diphenylphosphino)ethane] results in C—C bond formation and affords the title compound, *trans*-$[W(C_{24}H_{18}ClN_2P)Br(C_{26}H_{24}P_2)_2]PF_6\cdot 0.6CH_2Cl_2$. This complex, bis[1,2-bis(diphenylphosphino)ethane]bromido{chloro[3-(triphenylphosphonio)cyclopentadienylidene]diazomethanediido}tungsten hexafluorophosphate dichloromethane 0.6-solvate, contains the previously unknown ligand chloro[3-(triphenylphosphonio)cyclopentadienylidene]diazomethane. Evidence from bond lengths and torsion angles indicates significant through-ligand delocalization of electron density from tungsten to the nominally cationic phosphorus(V) centre. This structural analysis clearly demonstrates that the tungsten–dinitrogen unit is a powerful π-electron donor with the ability to transfer electron density from the metal to a distant acceptor centre through an extended conjugated ligand system. As a consequence, complexes of this type could have potential applications as nonlinear optical materials and molecular semiconductors.

Comment

Transition metal complexes containing extended conjugated organic ligands have the potential to display a wide range of novel electronic, magnetic and optical properties (Chisholm & Macintosh, 2005; Ceccon *et al.*, 2004; Schwab *et al.*, 1999) and thus to provide a basis for the development of molecular materials and devices (Low, 2005; Chisholm, 2000). One of the challenges in synthesizing such complexes is to design ligands that provide an extended conjugation pathway between multiple metal or metal/metalloid centres. Examples of ligands so far investigated for this purpose include polyethynylenes (Zheng *et al.*, 2004; Antonova *et al.*, 2004), 1,4-phenylenediethynylene (Nguyen *et al.*, 1999; Chawdhury *et al.*, 1998) and 4-ethynylpyridine (Ronson *et al.*, 2006; Zuo *et al.*, 2002). The use of dinitrogen-derived ligands, containing, for example, diazenido(1−), $M{=}N{=}N{-}R$, or diazoalkane, $M{\equiv}N{-}N{=}CR_2$, groups has been much less explored in this context, although we have recently shown that such complexes can have significant utility in the assembly of extended-chain polynuclear transition metal complexes (Colquhoun *et al.*, 2007).

The cationic dichlorodiazomethane complex *trans*-$[BrW(dppe)_2(N_2CCl_2)]^+$ [dppe is 1,2-bis(diphenylphosphino)ethane], (I), is readily obtained from *trans*-$W(dppe)_2(N_2)_2$ *via* the hydrazido(2−) complex *trans*-$[BrW(dppe)_2(NNH_2)]^+$, and undergoes facile replacement of one or both chloro substituents by a wide range of nitrogen- and oxygen-based nucleophiles (Colquhoun, 1984). We report here the first example of such a reaction involving a carbon-centred nucleophile, (triphenylphosphonio)cyclopentadienide, which (probably for steric reasons) replaces just one of the two chloro substituents at C to give *trans*-$[BrW(dppe)_2\{N_2C(Cl)(C_5H_3PPh_3)\}]^+$, isolated as the title hexafluorophosphate salt, (II).



(I) (II)

Two valence-bond structures, (*a*) and (*b*) (Fig. 1), may be drawn for the cation of (II), suggesting the possibility of extended delocalization of electron density between W and P *via* the π-system of the fully conjugated cyclopentadienylidene(chloro)diazomethane ligand. The structural features associated with such delocalization would be expected to include near coplanarity of the entire metal–ligand framework from W to P, some degree of equalization of bond distances between the exocyclic and endocyclic C atoms involved in delocalization, and some degree of shortening of the P—C(cyclopentadienylidene) bond relative to the adjacent P—C(phenyl) bonds. To determine whether such geometric effects can in fact be observed, a single-crystal X-ray study of complex (II) was undertaken.

Compound (II) crystallizes with discrete cations and anions in the form of a dichloromethane solvate. One of the phenyl rings of the triphenylphosphonium residue is rotationally disordered about the P5—C71 bond, but for clarity only one of the two orientations found is shown in Fig. 2. The metal–ligand system between atoms W1 and P5 exhibits a very high degree of coplanarity, with atoms W1 and N2 lying only 0.019 (3) and 0.026 (3) Å, respectively, out of the mean metal–ligand plane, and no other ligand atom being displaced from this plane by more than 0.01 Å (Fig. 3). Such coplanarity is certainly

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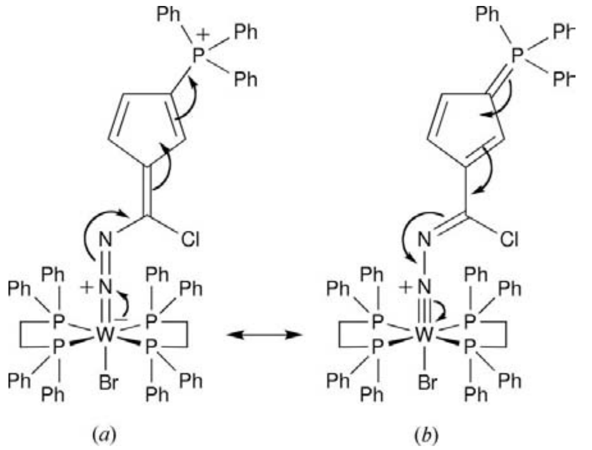

Figure 1
The potential delocalization of electron density in complex (II), as indicated by resonance between canonical forms (*a*) and (*b*). Form (*a*) represents a diazenido(1−) complex of W^{II} and form (*b*) a diazoalkane complex of W^{IV}.

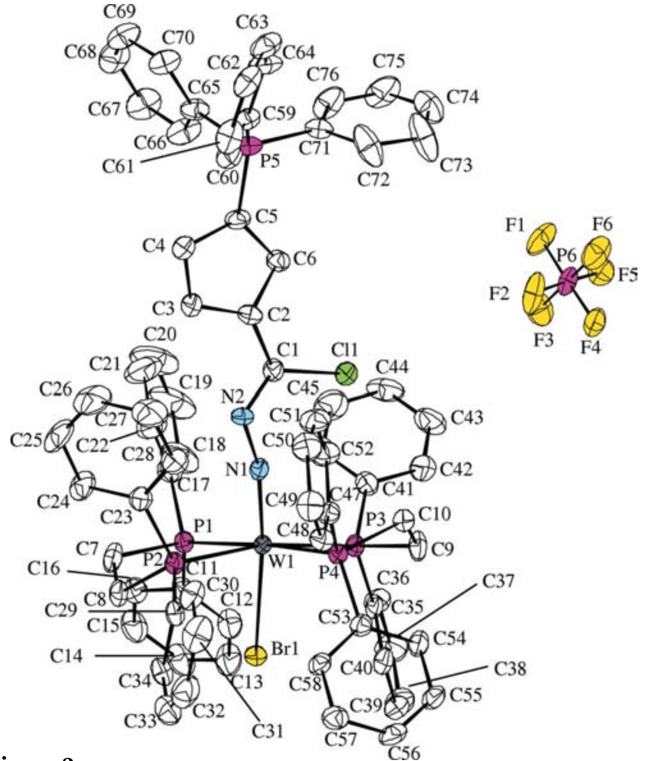

Figure 2
The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms and the minor disorder component of the C71–C76 ring have been omitted for clarity.

consistent with a degree of delocalization throughout the metal–ligand π system, and an analysis of bond lengths tends to confirm this.

Thus, although the pattern of C—C bond lengths (Table 1) is, at first sight, compatible simply with canonical form (*a*), there are a number of features of the structure which also seem to require a significant contribution from form (*b*). For example, the endocyclic C2—C6 and exocyclic C1—C2 bond lengths differ by only 0.014 (6) Å rather than showing the *ca* 0.18 Å difference expected between a single and a double C—C bond (Pauling, 1960). Moreover, the endocyclic C5═C6 double bond, which could be involved in long-range delocalization, is indeed lengthened slightly relative to the 'uninvolved' double bond C3—C4. Finally, the bond from P to the C_5 ring (P5—C5) is significantly shorter than the three adjacent P5—C bonds to phenyl rings [average 1.800 (5) Å], once again consistent with a contribution from canonical form (*b*). The W—N bond length, at 1.775 (4) Å, is longer than that normally associated with a W≡N triple bond at ~1.69 Å (Pyykko *et al.*, 2005), whilst the N—N bond distance, at 1.312 (5) Å, represents a bond order of *ca* 1.5 (Allen *et al.*, 1987). The W—N and N—N bond lengths thus also imply contributions to the structure from both canonical forms (*a*) and (*b*). The geometry at N1 is noticeably distorted from linearity [W1—N1—N2 = 164.5 (3)°] as a result of steric repulsions between the chloro substituent Cl1 and its adjacent diphosphine ligand.

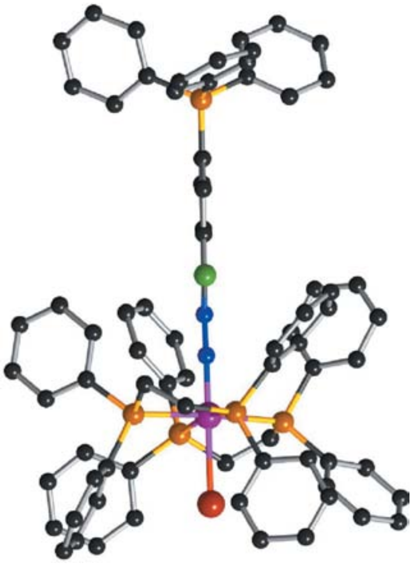

Figure 3
The structure of complex (II), showing the essential coplanarity of the extended diazoalkane ligand system. H atoms have been omitted for clarity.

The variations in bond lengths from those expected solely on the basis of canonical form (*a*), together with the coplanarity of the W1—N1—N2—C1(Cl1)—C_5H_3—P5 fragment and the torsion angles within the fragment, are thus fully compatible with delocalization of electron density throughout the metal–ligand π-system. Although the observed bond lengths do show some discrepancies from the bond orders suggested by Fig. 1 (notably the inequality of bonds C2—C3 and C3—C4), the overall pattern of bond lengths is clearly very much more consistent with the bond orders for this 'averaged' model than for either canonical form alone.

This structural analysis clearly demonstrates that the tungsten(II)–dinitrogen unit is a powerful π-electron donor, with the ability to transfer electron density from the metal to a distant acceptor centre through an extended conjugated ligand system. As a consequence, complexes of this type could have potential application as nonlinear optical materials and molecular semiconductors.

Experimental

(Triphenylphosphonio)cyclopentadienide (0.107 g, 0.329 mmol) and dry triethylamine (0.5 ml) were added, under nitrogen, to a stirred suspension of the dichlorodiazomethane complex, (I) (0.253 g. 0.192 mmol), in dichloromethane (20 ml). After 15 h, the deep-yellow–brown solution was extracted with water (3 × 30 ml), dried over magnesium sulfate and evaporated to half-volume. Slow addition of diethyl ether (10 ml) resulted in formation of dark olive-green crystals of (II), which were filtered off, washed with diethyl ether and dried under vacuum (0.256 g, 83% yield). Analysis found: C 54.62, H 4.35, N 1.73%; calculated for $C_{76}H_{66}BrClF_6N_2P_6W\cdot CH_2Cl_2$: C 54.68, H 4.15, N 1.66%; ^{1}H NMR (CDCl$_3$): δ 7.06–7.38 (*m*, 40H, PPh), 7.61–7.68 (*m*, 15H), 6.49–6.54 (*m*, 2H, Cp), 6.19–6.22 (*m*, 1H, Cp), 2.88 (*br d*, 8H, CH$_2$); ^{13}C NMR (CDCl$_3$): δ 128.30, 129.01, 129.97, 130.17, 130.27, 130.91, 133.61, 133.95, 134.71, 134.46, 134.51, 134.88, 135.02, 135.37, 120.48, 120.95, 122.74, 124.79, 31.62. Single crystals suitable for X-ray analysis were grown by vapour diffusion of diethyl ether into a solution of (II) in dichloromethane.

Crystal data

$[W(C_{24}H_{18}ClN_2P)Br(C_{26}H_{24}P_2)_2]$-$PF_6\cdot 0.6CH_2Cl_2$
M_r = 1657.27
Monoclinic, $P2_1/c$
a = 18.2621 (10) Å
b = 14.7060 (10) Å
c = 28.934 (2) Å
β = 98.236 (3)°
V = 7690.3 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.28 mm^{-1}
T = 150 (1) K
0.12 × 0.09 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min}$ = 0.79, $T_{\max}$ = 0.84
17372 measured reflections
17372 independent reflections
9841 reflections with $I > 3\sigma(I)$
$R_{\rm int}$ = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.037
S = 1.09
9841 reflections
875 parameters
24 restraints
H-atom parameters not refined
$\Delta\rho_{\max}$ = 1.01 e Å^{-3}
$\Delta\rho_{\min}$ = −0.70 e Å^{-3}

One of the phenyl rings attached to P5 was modelled as disordered over two positions. The C—C distances within each ring were restrained to 1.39 (1) Å. The occupancies of the two rings refined to 0.58 (3) (atoms C71–C76) and 0.42 (3) (atoms C720–C760). Not all the H atoms in the structure could be located in difference Fourier maps. H atoms were therefore positioned geometrically after each cycle of refinement, with C—H = 0.95 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The crystal structure contains a dichloromethane solvent molecule which was not sufficiently resolved in the electron-density map to enable it to be modelled with disordered atoms. The residual electron density was therefore modelled using the SQUEEZE routine available in *PLATON* (Spek, 2003). A total of 92 electrons were found in a solvent region of 527 Å^3 per unit cell, which corresponds to approximately 0.6 molecules of dichloromethane per formula unit.

Table 1
Selected geometric parameters (Å, °).

W1—Br1	2.5927 (5)	N2—C1	1.285 (6)
W1—P1	2.5383 (13)	Cl1—C1	1.757 (5)
W1—P2	2.5077 (12)	C1—C2	1.426 (6)
W1—P3	2.5543 (12)	C2—C3	1.427 (7)
W1—P4	2.5146 (13)	C2—C6	1.412 (6)
W1—N1	1.775 (4)	C3—C4	1.356 (7)
P5—C5	1.736 (5)	C4—C5	1.445 (7)
N1—N2	1.312 (5)	C5—C6	1.386 (7)
W1—N1—N2	164.5 (3)	C3—C2—C6	108.0 (4)
N1—N2—C1	126.0 (4)	C2—C3—C4	108.6 (5)
Cl1—C1—N2	121.5 (4)	C3—C4—C5	107.7 (4)
Cl1—C1—C2	117.4 (4)	C4—C5—P5	124.6 (4)
N2—C1—C2	121.0 (4)	C4—C5—C6	108.4 (4)
C1—C2—C3	123.9 (4)	P5—C5—C6	126.9 (4)
C1—C2—C6	128.2 (5)	C2—C6—C5	107.2 (4)
Br1—W1—N1—N2	1 (6)	C2—C6—C5—P5	179.3 (6)
W1—N1—N2—C1	180 (2)	N2—C1—C2—C3	−1.4 (11)
N1—N2—C1—Cl1	−2.4 (12)	C1—C2—C3—C4	179.9 (6)
N2—C1—C2—C6	179.5 (7)	C2—C3—C4—C5	1.1 (8)
C1—C2—C6—C5	179.5 (7)	C3—C4—C5—C6	−0.9 (6)

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3171). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Antonova, A. B., Bruce, M. I., Elis, B. G., Gaudio, M., Humphrey, P. A., Jevric, M., Melino, G., Nicholson, B. K., Perkins, G. J., Skelton, B. W., Stapleton, B., White, A. H. & Zaitseva, N. N. (2004). *Chem. Commun.* pp. 960–961.

Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.

Ceccon, A., Santi, S., Orian, L. & Bisello, A. (2004). *Coord. Chem. Rev.* **248**, 683–724.

Chawdhury, N., Kohler, A., Friend, R. H., Younus, M., Long, N. J., Raithby, P. R. & Lewis, J. (1998). *Macromolecules*, **31**, 722–727.

Chisholm, M. H. (2000). *Acc. Chem. Res.* **3**, 53–61.

Chisholm, M. H. & Macintosh, A. M. (2005). *Chem. Rev.* **105**, 2949–2976.

Colquhoun, H. M. (1984). *Acc. Chem. Res.* **17**, 23–28.

Colquhoun, H. M., Chan, Y. F., Cardin, C. J., Drew, M. G. B., Gan, Y., El Kader, K. A. & Whittle, T. R. (2007). *Dalton Trans.* pp. 3864–3867.

Low, P. J. (2005). *Dalton Trans.* pp. 2821–2824.

Nguyen, P., Gómez-Elipe, P. & Manners, I. (1999). *Chem. Rev.* **99**, 1515–1548.

Nonius (2001). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., pp. 221–241. Ithaca: Cornell University Press.

Pyykko, P., Riedel, S. & Patzschke, M. (2005). *Chem. Eur. J.* **11**, 3511–3520.

Ronson, T. K., Lazarides, T., Adams, H., Pope, S. J. A., Sykes, D., Faulkner, S., Coles, S. J., Hursthouse, M. B., Clegg, W., Harrington, R. W. & Ward, M. D. (2006). *Chem. Eur. J.* **36**, 9299–9313.

Schwab, P. F. H., Levin, M. D. & Michl, J. (1999). *Chem. Rev.* **99**, 1863–1933.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.

Zheng, Q. L., Hampel, F. & Gladysz, J. A. (2004). *Organometallics*, **23**, 5896–5899.

Zuo, J. L., Herdtweck, E., de Biani, F. F., Santos, A. M. & Kuhn, F. E. (2002). *New J. Chem.* **26**, 889–894.