Organoimido Complexes of Tungsten(IV) containing π-Alkene and π-Acetylene Ligands. The *X*-Ray Crystal Structure of Dichloro(diphenylacetylene)phenylimidobis(trimethylphosphine)tungsten(IV), [$WCl_2(NPh)(PhC{\equiv}CPh)(PMe_3)_2$]

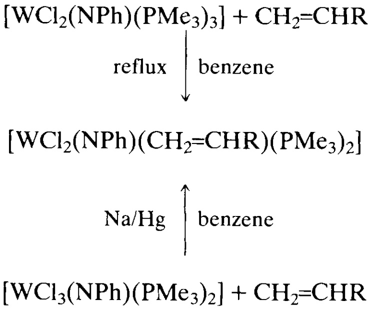
George R. Clark, Alastair J. Nielson,* Clifton E. F. Rickard, and David C. Ware

Department of Chemistry, University of Auckland, Private Bag, Auckland, New Zealand

Reduction of [$WCl_3(NPh)(PMe_3)_2$)] under ethylene or propene leads to the complexes [$WCl_2(NPh)(\pi$-alkene$)(PMe_3)_2$], and reaction of [$WCl_2(NPh)(PMe_3)_3$] with a variety of acetylenes gives [$WCl_2(NPh)(\pi$-acetylene$)(PMe_3)_2$]; the structure of [$WCl_2(NPh)(PhC{\equiv}CPh)(PMe_3)_2$] has been established by *X*-ray crystallography.

The co-ordination of unsaturated molecules to group VI transition metal oxo complexes[1] is a recent advance in the search for compounds which serve as models for metal-catalysed oxidation reactions. However little is known about related complexes which contain both an unsaturated organic ligand and the multiply bonded organoimido function (M≡NR), despite the implication of such groups in aziridination[2] and ammoxidation reactions.[3]

We find that organoimido complexes of tungsten(IV) containing a π-alkene ligand can be prepared by phosphine exchange or reduction reactions carried out under ethylene or propene according to Scheme 1. High yields of the π-alkene complexes were obtained by the reduction process whereas the phosphine exchange reaction did not proceed to completion. I.r. and n.m.r. spectral data indicated that the ethylene complex contained *cis*-chloro and *trans*-phosphine ligands and



$$\begin{tikzcd}[WCl_2(NPh)(PMe_3)_3] + CH_2{=}CHR \arrow[d, "\text{reflux}"', "\text{benzene}"] \\ [WCl_2(NPh)(CH_2{=}CHR)(PMe_3)_2] \\ [WCl_3(NPh)(PMe_3)_2] + CH_2{=}CHR \arrow[u, "\text{Na/Hg}", "\text{benzene}"'] \end{tikzcd}$$

Scheme 1. R = H or Me.

the propene complex contained both *cis*-chloro and *cis*-phosphine ligands.† In the latter complex the propene ligand adopts two different orientations as indicated by two distinct sets of CH_2, CH, and CH_3 carbon resonances in the $^{13}C\{^1H\}$ n.m.r. spectrum and two doublet of doublet sets in the $^{31}P\{^1H\}$ n.m.r. spectrum.

Attempts to reduce the complexes $[WCl_3(NPh)(P)_2]$ [(P) = PPh_3, $PMePh_2$] with sodium amalgam in benzene under ethylene or propene were not successful but reduction of $[WCl_3(NPh)(PMe_2Ph)_2]$ under propene gave $[WCl_2(NPh)(CH_2{=}CHMe)(PMe_3)_2]$ suggesting that steric properties associated with the phosphine ligand play a role in the success of the reaction. Similarly, steric influences associated with the alkene appear important as reductions of $[WCl_3(NPh)(PMe_3)_2]$ in the presence of $Ph_2C{=}CH_2$, $PhCH{=}CH_2$, cyclohexene, $MeCH{=}CHCO_2Me$, and $MeCH{=}CHCOMe$ produced intractable materials and some $[WCl_2(NPh)(PMe_3)_3]$. Also, phosphine substitutions did not take place when these alkenes were refluxed with $[WCl_2(NPh)(PMe_3)_3]$ in benzene.

π-Acetylene complexes can similarly be prepared by phosphine exchange but the reduction reaction was not successful. Refluxing the complexes $[WCl_2(NPh)(P)_3]$ [(P) = PMe_3, PMe_2Ph] with excess of diphenylacetylene in benzene gave the complexes $[WCl_2(NPh)(PhC{\equiv}CPh)(P)_2]$ for which i.r. and n.m.r. spectral data indicated a *cis*-chloro,*trans*-phosphine structure. With the complexes $[WCl_2(NR)(PMe_3)_3]$ (R = Ph, Pr^i), phenylacetylene gave the *cis*-chloro, *cis*-phosphine complexes $[WCl_2(NR)(PhC{\equiv}CH)(PMe_3)_2]$ while a similar reaction of $[WCl_2(NPh)(PMe_3)_3]$ and acetylene led to the *cis*-chloro, *trans*-phosphine complex $[WCl_2(NPh)(HC{\equiv}CH)(PMe_3)_2]$. $Me_3SiC{\equiv}CSiMe_3$ and $MeO_2CC{\equiv}CCO_2Me$ did not replace a phosphine ligand under reflux conditions in benzene or toluene.

The $^{13}C\{^1H\}$ n.m.r. spectra of the acetylene complexes recorded at 100 MHz showed a variety of couplings to phosphorus-31 and tungsten-183.‡ The acetylenic carbon resonances were significantly lower than those reported for other acetylene complexes so that resonance positions alone could not be used to establish with certainty whether the acetylene ligands were acting as 2- or 4-electron donors.[4,5]

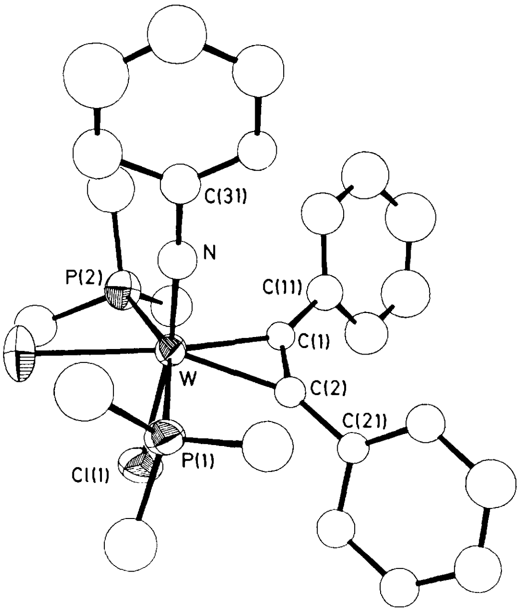


Figure 1. Molecular structure of $[WCl_2(NPh)(PhC{\equiv}CPh)(PMe_3)_2]$. Important averaged bond lengths (Å) and bond angles (°): W–C(1) 2.128(20), W–C(2) 2.123(21), W–Cl(1) 2.503(8), W–Cl(2) 2.515(8), W–N 1.770(14), C(1)–C(2) 1.26(2); W–N–C(31) 176.3(1.5), W–C(1)–C(11) 147.3 (1.4), W–C(2)–C(21) 145.7 (1.3), N–W–C(1) 94.9(7), N–W–C(2) 104.6(7), C(1)–C(2)–C(21) 140.9 (2.1), C(2)–C(1)–C(11) 139.9 (2.1), P(1)–W–P(2) 157.9(2), N–W–Cl(1) 170.6(6), P(1)–W–N 87.6(4), P(2)–W–N 99.5(5).

An *X*-ray crystal structure determination of $[WCl_2(NPh)(PhC{\equiv}CPh)(PMe_3)_2]$ was carried out.§ The asymmetric unit contains two crystallographically distinct, but structurally similar molecules. The structure of one of these molecules (Figure 1) shows a distorted octahedral geometry about tungsten, with *cis*-chloro ligands, *trans*-phosphines, and a *cis*-orientation of the diphenylacetylene and phenylimido ligands. The diphenylacetylene ligand is accommodated by a twist about the W–acetylene axis [N–W–C(1) 94.9(7)°, N–W–C(2) 104.6(7)°] and there is a concomitant reverse twist of the phosphines [P(1)–W–N 87.6(4)°, P(2)–W–N 99.5(5)°]. In addition the PMe_3 ligands are bent away from the diphenylacetylene ligand [P(1)–W–P(2) 157.9(2)°].

---

† For $[WCl_2(NPh)(CH_2{=}CH_2)(PMe_3)_2]$: ν(W–Cl) 284 and 245 cm^{-1}; ^1H n.m.r.: PMe_3 triplet at δ 1.67. For $[WCl_2(NPh)(CH_2{=}CHMe)(PMe_3)_2]$: ν(W–Cl) 275 and 250 cm^{-1}; ^1H n.m.r.: PMe_3 doublets at δ 1.80.

‡ For example, in the *cis*-chloro,*cis*-phosphine complex $[WCl_2(NPh)(PhC{\equiv}CH)(PMe_3)_2]$ both acetylenic carbons appear as a doublet of doublets [$^2J(PhC\text{–}P_{trans})$ 15.6, $^2J(HC\text{–}P_{trans})$ 22.0, $^2J(PhC\text{–}P_{cis})$ 4.9, $^2J(HC\text{–}P_{cis})$ 5.3 Hz] and both are coupled to ^{183}W [$^1J(PhC\text{–}^{183}W)$ 31.2, $^1J(HC\text{–}^{183}W)$ 23.2 Hz]. The phenylimido ligand *ipso* and *ortho* carbons and the phenylacetylene *ipso* carbon each appear as a triplet ($^3J_{C\text{–}P}$ 2.3, $^4J_{C\text{–}P}$ 1.9, and $^3J_{C\text{–}P}$ 3.4 Hz, respectively) with only the phenylimido *ipso* carbon showing coupling to ^{183}W [$^2J(C\text{–}^{183}W)$ 36.4 Hz].

§ *Crystal data* for $[WCl_2(NPh)(PhC{\equiv}CPh)(PMe_3)_2]$: $C_{26}H_{33}Cl_2NP_2W$, *M* = 676.28, triclinic, space group $P\bar{1}$, *a* = 16.618(2), *b* = 16.869(3), *c* = 11.591(2) Å, α = 99.92(1), β = 90.58(1), γ = 63.81(1)°, *U* = 2863.9 $Å^3$, *F*(000) = 1336, D_c = 1.568 g cm^{-3}, *Z* = 4, μ(Mo-K_α) = 45.76 cm^{-1}. Intensity data were recorded on a Nonius CAD4 diffractometer with Mo-K_α radiation and corrected for Lorentz, polarisation, and absorption effects. The structure was solved from Patterson and heavy-atom electron density syntheses and refined by full-matrix least-squares, omitting hydrogens, with tungsten, chlorine, and phosphorus atoms anisotropic, to an *R* value of 0.028 for 1392 independent reflections for which $I > 2.5\sigma(I)$. It should be noted that relationships exist between the co-ordinates in the two molecules. The authors could find no evidence for higher symmetry, but it is possible that the structure has been determined on a twinned crystal. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The linear W–N–C_{imido} bonds [angle 176.3(1.5)°] and W–N_{imido} bond length [1.770(14) Å] indicate that the phenylimido ligand acts as a 4-electron donor to tungsten while the geometry associated with the co-ordinated diphenylacetylene ligand [W–C bond lengths 2.128(20) and 2.123(21) Å, C≡C bond length 1.26(2) Å, C–C–Ph bond angles 140.9 (2.1) and 139.9 (2.1)°] indicates a 2-electron donor. As a consequence there is no competitive π-donation between the two *cis*-ligands as has been observed in $[Mo(Ntol)(dmac)(S_2CNEt_2)_2]$ (tol = *p*-tolyl, dmac = $MeO_2CC{\equiv}CCO_2Me$)[6] where the bond orders of the imido and acetylene ligands are each approximately 2.5. The +4 oxidation state of tungsten is retained in the present complex, there being no structural features suggesting a diphenylacetylene dianion and oxidation of the metal to W^{VI}. Further, the W–Cl bond *trans* to the imido function is not significantly lengthened which is in accord with that observed in other tungsten(IV) phenylimido complexes.[7]

Initial studies of the reactivity of these complexes indicate that the organoimido ligand does not insert into the π-alkene or π-acetylene–metal bond. The acetylene complexes are air stable and do not lose the unsaturated ligand as has been observed for the molybdenum complexes $[Mo(O)(RC{\equiv}CR)(S_2CNEt_2)_2]$ (R = H, Ph, Et).[1a] The complexes prepared represent a new class of d^2 tungsten organoimido complexes and complement those d^0 organoimido complexes which also contain a *cis*-oxo,[8] an alkylidene,[9] or an organoimido ligand.[10]

Received, 5th April 1988; Com. 8/01321G

References

1 (a) F.-M. Su, C. Cooper, S. J. Geib, A. L. Rheingold, and J. M. Mayer, *J. Am. Chem. Soc.*, 1986, **108**, 3545; (b) G. J.-J. Chen, J. W. McDonald, and W. E. Newton, *Organometallics*, 1985, **4**, 422; (c) M. A. Bennett and I. W. Boyd, *J. Organomet. Chem.*, 1985, **290**, 165; (d) J. L. Templeton, P. B. Winston, and B. C. Ward, *J. Am. Chem. Soc.*, 1981, **103**, 7713; (e) W. E. Newton, J. W. McDonald, J. L. Corbin, L. Ricard, and R. Weiss, *Inorg. Chem.*, 1980, **19**, 1997.

2 D. Mansuy, J.-P. Mahy, A. Durreault, G. Bedi, and P. Battioni, *J. Chem. Soc., Chem. Commun.*, 1984, 1161; J. T. Groves and T. Takahashi, *J. Am. Chem. Soc.*, 1983, **105**, 2073.

3 B. C. Gates, J. R. Katzer, and G. C. A. Schuit, 'Chemistry of Catalytic Processes,' McGraw-Hill, New York, 1979, p. 325.

4 E. C. Walborsky, D. E. Wigley, E. Roland, J. C. Dewan, and R. R. Schrock, *Inorg. Chem.*, 1987, **26**, 1615.

5 J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc.*, 1980, **102**, 3288.

6 D. D. Devore and E. A. Maatta, *Inorg. Chim. Acta*, 1986, **112**, 87.

7 D. C. Bradley, M. B. Hursthouse, K. M. A. Malik, A. J. Nielson, and R. L. Short, *J. Chem. Soc., Dalton Trans.*, 1983, 2651.

8 G. R. Clark, A. J. Nielson, and C. E. F. Rickard, *Polyhedron*, 1988, **7**, 117; D. C. Bradley, M. B. Hursthouse, K. M. A. Malik, and A. J. Nielson, *J. Chem. Soc., Chem. Commun.*, 1981, 103.

9 S. M. Rocklage, R. R. Schrock, M. R. Churchill, and H. J. Wasserman, *Organometallics*, 1982, **1**, 1332.

10 B. R. Ashcroft, D. C. Bradley, G. R. Clark, R. J. Errington, A. J. Nielson, and C. E. F. Rickard, *J. Chem. Soc., Chem. Commun.*, 1987, 170; B. R. Ashcroft, A. J. Nielson, D. C. Bradley, R. J. Errington, M. B. Hursthouse, and R. L. Short, *J. Chem. Soc., Dalton Trans.*, 1987, 2059; D. C. Bradley, R. J. Errington, M. B. Hursthouse, R. L. Short, B. R. Ashcroft, G. R. Clark, A. J. Nielson, and C. E. F. Rickard, *J. Chem. Soc., Dalton Trans.*, 1987, 2067; A. J. Nielson, *Polyhedron*, 1987, **6**, 1657.