JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 8
1984

Formation of a Tetrahedral WC_3 Framework from a Cyclic WC_3 (Tungstenacyclobutadiene) System *via* Attack on Tungsten by Nitrogen-donor Ligands: *X*-Ray Study of $W[C_3Me_2(Bu^t)][Me_2N(CH_2)_2NMe_2]Cl_3$

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The tungstenacyclobutadiene complex $W[C_3Me_2(Bu^t)]Cl_3$ reacts with $Me_2N(CH_2)_2NMe_2$ to form the 1 : 1 adduct $W[C_3Me_2(Bu^t)][Me_2N(CH_2)_2NMe_2]Cl_3$; a single-crystal *X*-ray diffraction study of this product shows it to possess a 'tungstenatetrahedrane'-like core with short W–C distances [2.040(7), 2.115(7), 2.133(7) Å].

We have shown previously that tungsten alkylidyne complexes react with disubstituted acetylenes to yield tungstenacyclobutadiene complexes; $W[C_3Me_2(Bu^t)]CL_3$,[1] $W[C_3Et_3][o\text{-}2,6\text{-}C_6H_3(Pr^i)_2]_3$,[2] and $W[C_3Et_3][OCH(CF_3)_2]_3$[3] each contain a planar, delocalized WC_3 ring whereas $W(\eta^5\text{-}C_5H_5)[CPhC(Bu^t)CPh]Cl_2$ contains a non-planar localized fluxional WC_3 ring.[4] Certain trialkoxytungstenacyclobutadiene complexes are catalysts for the metathesis of disubstituted alkynes. In contrast to this, terminal alkynes are not metathesized, due (we believe) to the production of stable deprotonated tungstenacyclobutadiene complexes such as $W(\eta^5\text{-}C_5H_5)[C_3(Bu^t)_2]Cl$, the crystal structure of which has been reported.[5] We now report a novel reaction between the tungstenacyclobutadiene complex $W[C_3Me_2(Bu^t)]Cl_3$ and nitrogen-donor ligands.

Treatment of a CH_2Cl_2 solution of $W[C_3Me_2(Bu^t)]Cl_3$ with rather more than two equivalents of pyridine (py) produces an essentially quantitative yield of $W[C_3Me_2(Bu^t)](py)_2Cl_3$. Two isomers are present, one of which has equivalent pyridine ligands (*sym* isomer), while the other has inequivalent pyridines (*asym* isomer). At room temperature one of the pyridine ligands in the *asym* isomer appears to be labile. The ^{1}H n.m.r. spectrum reported below† was taken at −20 °C where the broadened pyridine resonances were sharp (there was no further change down to −60 °C). Similar conditions, using the bidentate ligand $Me_2N(CH_2)_2NMe_2$ in place of pyridine, were used to prepare $W[C_3Me_2(Bu^t)]$ $[Me_2N(CH_2)_2NMe_2]Cl_3$ in essentially quantitative yield;‡ this complex exists as a single isomer and its structure has been determined by a single-crystal *X*-ray diffraction study.§

Crystal data: $C_{15}H_{31}Cl_3N_2W$, $M = 529.6$, monoclinic, space group $P2_1/n$, $a = 10.982(2)$, $b = 13.257(4)$, $c = 13.957(4)$ Å, $\beta = 105.33(2)^\circ$, $U = 1960(1)$ Å^3, $D_c = 1.80$ g cm^{-3}, $Z = 4$, $\mu(\text{Mo-}K_\alpha) = 66.4$ cm^{-1}. Diffraction data were collected with a Syntex $P2_1$ automated four-circle diffractometer[6] using Mo-K_α radiation. All non-hydrogen atoms were accurately located and hydrogen atoms were included in calculated positions.[7] Convergence was reached with $R = 3.8\%$ for all 2576 independent data with $4.5^\circ < 2\theta < 45.0^\circ$. [$R = 2.6\%$ for those 2088 reflections with $|F_O| > 6\sigma(|F_O|)$]. The resulting structure is shown in Figure 1 and may formally be represented by (I). The asymmetric isomer of $W[C_3Me_2(Bu^t)](py)_2Cl_3$ is most probably that shown as (II), while the *sym*-isomer probably has a related structure with both pyridine ligands in the equatorial plane.

The tungsten atom in $W[C_3Me_2(Bu^t)][Me_2N(CH_2)_2NMe_2]Cl_3$ has a pseudo-octahedral co-ordination geometry. The C_3 ring and N(1) occupy apical positions while the three chloride ligands have a meridional disposition in the equatorial plane, which is completed by N(2). The W–N(1) distance of 2.492(6) Å is substantially longer than the W–N(2) distance of 2.325(6) Å {this is compatible with the lability noted for one pyridine ligand in the *asym*-

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† ^{1}H n.m.r. (CD_2Cl_2, 250 MHz, −20 °C) δ 9.02 (d, 4, py, *sym*), 8.62 and 8.52 (d, 2 each, py, *asym*), 7.80, 7.67, 7.41, and 7.15 (all other py resonances combined), 4.11 (s, 6, CMe, *asym*), 3.72 (s, 6, CMe, *sym*), 1.15 (s, 9, $CCMe_3$, *asym*), 0.99 (s, 9, $CCMe_3$, *sym*). ^{13}C n.m.r. assignments are not separated according to isomer. The metallacycle ring carbons were picked out from a gated {^{1}H} n.m.r. spectrum. ^{13}C{^{1}H} n.m.r. (CD_2Cl_2, 67.9 MHz) δ 171.8, 144.6, 143.1, and 126.2 ($\mathit{C}CMe_3$ and $\mathit{C}Me$), 153.3, 152.6, 151.0, 140.1, 139.3, 138.3, 125.1, 124.3, and 123.4 (py), 39.2 ($C\mathit{C}Me_3$), 32.3 and 32.1 ($CC\mathit{Me}_3$), 30.1 ($C\mathit{C}Me_3$), 16.5 and 13.6 p.p.m. ($C\mathit{Me}$).

‡ ^{1}H n.m.r. (CD_2Cl_2, 250 MHz, 20 °C) δ 4.61 (s, 6, CMe), 2.86 and 2.69 [s with broad resonances underneath, 8 each, $\mathit{Me}_2N(\mathit{CH}_2)_2N\mathit{Me}_2$], 1.27 (s, 9, $CCMe_3$). At −70 °C: δ 4.53 and 4.36 (br. s, 3 each, CMe), 2.76 and 2.61 [br. s, 16 total, $\mathit{Me}_2N(\mathit{CH}_2)_2N\mathit{Me}_2$], 1.15 (s, 9, $CCMe_3$).

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

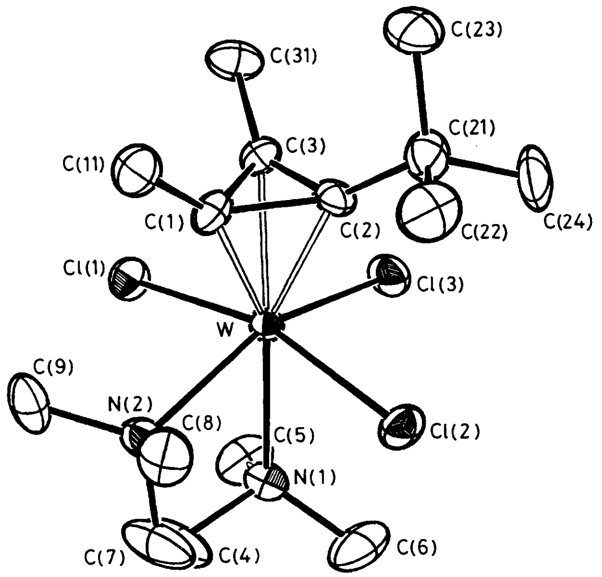
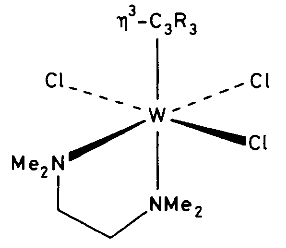
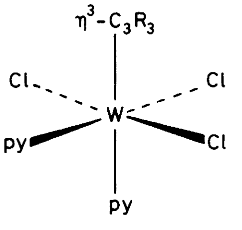


Figure 1. Molecular geometry of $W[C_3Me_2(Bu^t)][Me_2N(CH_2)_2NMe_2]Cl_3$ (ORTEP diagram; 30% probability ellipsoids, with hydrogen atoms omitted for clarity).



(I)



(II)

$W[C_3Me_2(Bu^t)](py)_2Cl_3$ molecule}. The W–Cl distances are essentially equivalent [W–Cl(1) 2.425(2), W–Cl(2) 2.399(2), W–Cl(3) 2.433(2) Å]. All equatorial ligands lie *below* the ideal equatorial plane [*i.e.*, *cis* N(1)–W–ligand angles are acute, *viz.*, N(1)–W–N(2) 75.8(2), N(1)–W–Cl(1) 80.5(1), N(1)–W–Cl(2) 81.2(1), and N(1)–W–Cl(3) 79.1(1)°].

The three carbon atoms of the C_3 ring are rather close to the tungsten atom [W–C(1) 2.040(7), W–C(2) 2.115(7), W–C(3) 2.133(7), W · · · centroid 1.920 Å], especially when compared to the predicted W–C(sp^3) σ-bond distance of 2.20 Å {based on W–Cl(av.) 2.42 Å in this complex, *r*(Cl) = 0.99 and *r*[C(sp^3)] = 0.77 Å}. Carbon–carbon distances within the ring vary significantly [C(1)–C(2) 1.547(10), C(1)–C(3) 1.432(10), C(2)–C(3) 1.383(9) Å], while ring-to-substituent distances are all similar to one another [C(1)–C(11) 1.490(11), C(2)–C(21) 1.503(10), C(3)–C(31) 1.493(10) Å]. The substituents are all bent back from the plane of the ring (away from the metal atom) such that < centroid–C(1)–C(11) = 136.5, < centroid–C(2)–C(21) = 144.7, and < centroid–C(3)–C(31) = 154.4°.

Both the n.m.r. data (showing that the C_3 ring does not freely rotate at −80 °C) and the structural data [short W–C ring distances, strong *trans*-lengthening effect of the η^3-$C_3Me_2(Bu^t)$ ligand on the W–N(1) bond, bending back of substituents] militate against regarding the C_3-ligand as a simple two-electron donating η^3-cyclopropenium ligand and in favour of it being more strongly bound to the metal atom. Possibilities are that the complex contains a true tungstenatetrahedrane core (*i.e.*, W^{VI} with a $C_3R_3{}^{3-}$ ligand) or, more likely, that it is a cyclopropenyl complex (*i.e.*, W^{IV} with a $C_3R_3{}^{-}$ ligand).

In closing we note that the related η^3-cyclopropenium species $Mo(C_3Ph_3)(CO)_2(bipy)Br$ (bipy = 2,2′-bipyridine) has a Mo · · · centroid distance of 2.06 Å and Mo–C(η^3-C_3Ph_3) distances of 2.193(18)—2.262(22) Å.[8]

This work was supported by the National Science Foundation.

Received, 30th January 1984; Com. 128

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