A New Chelating Ligand: Co-ordination Chemistry of $[W(CO)(Ph_2PC{\equiv}CPPh_2)(S_2CNEt_2)_2]$

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The adoption of a *cis*-bent structure by bis(diphenylphosphino)acetylene (dppa) in $[W(CO)(dppa)(S_2CNEt_2)_2]$ facilitates the formation of $[(Et_2NCS_2)_2(OC)W(\mu\text{-dppa})Co_2(\mu\text{-}CO)_2(CO)_4]$, in which the dppa moiety bridges a cobalt–cobalt bond, and $[(Et_2NCS_2)_2(OC)W(\mu\text{-dppa})Mo(CO)_4]$, in which the dppa moiety is chelated to a molybdenum centre.

It is well established that co-ordination of an alkyne to a transition metal results in two basic structural modifications of the carbon skeleton.[1] The acetylenic bond distance increases, reflecting the weakening of the bond upon co-ordination, and the skeleton distorts to give a *cis*-bent structure.[2] The bend-back angle usually lies in the range 130—170° and there is apparently little correlation between this deviation from linearity and the nature of the bonding interaction with the metal.[3] In this Communication we demonstrate that this geometric change can have significant effects upon chemical reactivity.

Bis(diphenylphosphino)acetylene (dppa) forms a variety of transition metal complexes *via* co-ordination of the two phosphorus centres.[4] The linear nature of dppa precludes chelation to a mono- or poly-nuclear metal centre and the ligand links non-bonded metals.[5] For example, dppa reacts with $[Co_2(CO)_8]$ to form $[\{Co_2(CO)_7\}_2dppa]$ in which two $Co_2(CO)_7$ moieties are linked by dppa.[6] Less commonly dppa co-ordinates through the acetylenic bond as observed in (**1**) in which the dppa is no longer linear.[7]

Reaction of (**1**)[7] with $[Co_2(CO)_8]$ in CH_2Cl_2 at room temperature affords yellow (**2**) in *ca.* 46% yield. The distortion caused by ligation of the acetylenic bond has enabled dppa to span the Co–Co bond in an analogous fashion to bis(diphenylphosphino)methane and related ligands.[8] The carbonyl i.r. absorptions of (**2**)[†] are analogous to those

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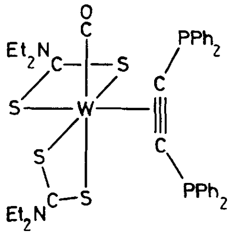
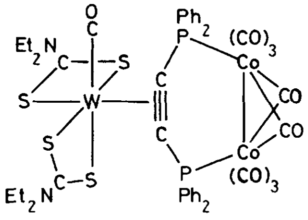
[†] *Selected spectroscopic data* for compound (**2**): i.r. ν_{CO} (toluene) 2038s, 2003s, 1982vs, 1966m, 1938m, 1824m, 1814m, and 1791w cm^{-1}; n.m.r.: $^{13}C\text{-}\{^1H\}(CD_2Cl_2–CH_2Cl_2)$, δ 235.8 (s, WCO), 218.6 (s, $C{\equiv}C$), 215.2 (s, CoCO), 212.2, 200.0 (2 × s, S_2CNEt_2) 136—128 (m, Ph), 46.4, 44.9, 44.7, 44.6 (4 × s, CH_2), and 13.1, 12.6 (×2), 12.2 (4 × s, CH_3); $^{31}P\text{-}\{^1H\}$ $(CD_2Cl_2–CH_2Cl_2)$, 213 K, δ +31.4 (d, J_{PP} 91 Hz) and +21.3 (d, J_{PP} 91 Hz) p.p.m.

Compound (**3**): i.r. ν_{CO} (toluene) 2020s, 1950m, 1923s, 1914vs, and 1890m cm^{-1}; n.m.r.: $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2), δ 236.1 (d, $C{\equiv}C$, J_{PC} 9 Hz, J_{WC} 37 Hz), 233.3 (WCO, J_{WC} 135 Hz), 217.5 [dd, *trans*-$Mo(CO)_2$, J_{PC} 7 and 29 Hz], 211.9 (S_2CNEt_2), 209.1 [t, *cis*-$Mo(CO)_2$, J_{PC} 9 Hz], 198.8 (S_2CNEt_2), 135—127 (m, Ph), 45.8, 44.2, 44.0, 43.7 (4 × s, CH_2), and 12.1, 11.4, 11.3, 11.2 (4 × s, CH_3), $^{31}P\text{-}\{^1H\}(CD_2Cl_2$, 213 K), δ +48.5 (d, J_{PP} 4 Hz) and +44.2 (d, J_{PP} 4 Hz) p.p.m.

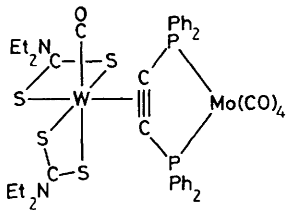
Compound (**4**): i.r. ν_{CO} (toluene) 2047s, 1978sh, 1964s, 1947vs, and 1933s cm^{-1}; n.m.r.: $^{13}C\text{-}\{^1H\}$ $(CD_2Cl_2–CH_2Cl_2)$, δ 238.2 (s, WCO) 217.9 (d, $C{\equiv}C$, J_{PC} 14 Hz), 214.8 (d, FeCO, J_{PC} 15 Hz), 211.6, 199.4 (2 × s, S_2CNEt_2), 138—128 (m, Ph), 46.4, 45.1, 44.9, 44.8 (4 × s, CH_2), and 13.3, 12.7 (×2), 12.3 (4 × s, CH_3); $^{31}P\text{-}\{^1H\}$ $(CD_2Cl_2–CH_2Cl_2$, 182 K), δ +81.9 (s) and +74.0 (s) p.p.m.



(1)



(2)



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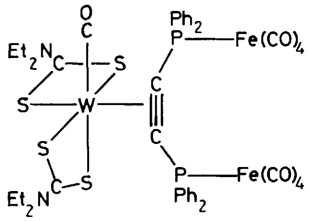

(4)

reported for a range of $[Co_2(\mu-L_2)(\mu-CO)_2(CO)_4]$ complexes[9] with the addition of a band at 1938 cm^{-1} corresponding to the tungsten carbonyl which appears at 1931 cm^{-1} in the spectrum of (**1**). N.m.r. spectra† of (**2**) are also easily interpreted by comparison with those of (**1**) and various $[Co_2(\mu-L_2)(\mu-CO)_2(CO)_4]$ complexes.[10] The $^{13}C-\{^1H\}$ n.m.r. resonance of the tungsten carbonyl occurs at δ 235.8 [δ 237.9 in (**1**)] while a single broad peak is observed for the fluxional cobalt carbonyls at δ 215.2. The alkyne is rotating on the n.m.r. timescale at room temperature in analogous fashion to (**1**) and a single broad resonance for the acetylenic carbons is observed at δ 218.6.[7] This fluxional process is also observed in the $^{31}P-\{^1H\}$ n.m.r. spectra. At room temperature a single broad resonance is observed at δ +23.7 p.p.m. which upon lowering the temperature to 213 K becomes two sharp doublets at δ +31.4 and +21.3 p.p.m. (J_{PP} 91 Hz).

In order to establish whether it is possible for the co-ordinated dppa to act as a chelating ligand, in an analogous manner to bis(diphenylphosphino)ethane, complex (**1**) was reacted with *cis*-$[Mo(CO)_4(piperidine)_2]$.[11] In CH_2Cl_2 at room temperature the reaction affords pale green (**3**) in *ca.* 69% yield. The carbonyl i.r. absorptions of (**3**)† are analogous to those reported for *cis*-$[Mo(Ph_2PCH_2CH_2PPh_2)(CO)_4]$ (2020, 1925, 1912, 1894 cm^{-1})[12] with the addition of a band at 1950 cm^{-1} corresponding to the tungsten carbonyl. The $^{13}C-\{^1H\}$ n.m.r. spectrum of (**3**)† contains a resonance due to the tungsten carbonyl at δ 233.3 (J_{WC} 135 Hz) and resonances due to the molybdenum carbonyls, analogous to those reported for $[Mo(Ph_2PCH_2CH_2PPh_2)(CO)_4]$.[13] The acetylenic carbons produce a resonance at δ 236.1 (J_{PC} 9, J_{WC} 37 Hz) indicating alkyne rotation, which is again confirmed by recording the $^{31}P-\{^1H\}$ n.m.r. spectrum. At room temperature a single broad resonance is observed at δ +47.8 p.p.m. which upon lowering the temperature to 213 K becomes two sharp doublets at δ +48.5 and +44.2 p.p.m. (J_{PP} 4 Hz).

Compound (**1**) also reacts with $[Fe_2(CO)_9]$ to afford yellow (**4**) in *ca.* 69% yield which has been characterised by comparison of its spectroscopic† characteristics with (**1**) and $[Fe_2(\mu-dppm)(CO)_8]$.[14] The latter compound undergoes photolysis to form $[Fe_2(\mu-dppm)(\mu-CO)(CO)_6]$, containing an Fe–Fe bond.[14,15] Photolysis of (**4**) does not afford an analogous compound and is the subject of further investigation.

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