New Bonding Mode of (Dithioformato)phosphine Ligand: Synthesis, Reactivity and Crystal Structure of [W(CO)₅(PPh₂CS₂)]Et₄N

Kuang-Hway Yih, Ying-Chih Lin,* Ming-Chu Cheng and Yu Wang

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China

The phosphorus coordination of the diphenyl(dithioformato)phosphine ligand in [W(CO)₅(PPh₂CS₂)]Et₄N, 1 has been confirmed by an X-ray diffraction analysis; alkylation of 1 at the S atom results in the formation of W(CO)₅[PPh₂(CS₂R)], 4 in high yield.

The chemistry of a zwitterionic trialkylphosphonium dithiocarboxylate ligand, PR₃⁺CS₂⁻, with three possible coordination sites, has attracted considerable attention in recent years. Various bonding modes, which include monodentate coordination, bidentate coordination by chelation and, in dinuclear complexes, bridging coordination in different fashions, are known. On the other hand, the chemistry of anionic dialkyphosphinodithioformates, PR₂CS₂⁻, is much less studied. The zirconium complex Zr(η-C₅H₅)₂[η²-S₂CP(SiMe₃)₂]Cl is the only example reported in the litera-
ture. The two sulfur containing ligands bond to the metal centre exclusively through S-coordination in all of the reported complexes mentioned above. Herein we report a new coordination mode of the PR$_2$CS$_2^-$ ligand, which is bonded to the metal through phosphorus-coordination with a O,N-bonding mode.

Treatment of W(CO)$_6$(PPh$_2$H) with Bu$_3$Li and CS$_2$ in the presence of Et$_4$NBr afforded in 80% yield a red product, which was identified as [W(CO)$_6$(PPh$_2$CS$_2$)]Et$_4$N, I. Satisfactory spectroscopic and analytical data of I were obtained. In the $^{31}$P NMR spectrum of I, a resonance at $\delta$ 59.08 with a

† Selected spectroscopic data: $^1$H and $^{31}$C-(1H) NMR are recorded at 298 K in CD$_3$CN and given as $\delta$ relative to SiMe$_4$, $^{31}$P NMR data: H$_2$PO$_4$ external standard. For I: IR v/cm$^{-1}$ (KBr), v(CO): 2070 m, 1988 s, 1957 sh, 1911 vs. $^{31}$P NMR: 59.08 with a resonance at $\delta$ 59.08.

- 24.23 (238.24 Hz) indicates phosphorus bonding geometry but were not refined by least-squares refinements with $R_{int} = 0.028$. The structure was solved by using the heavy atom method, a series of difference Fourier maps and refined by least-squares refinements with $R = 0.028$ and $R_w = 0.025$. Hydrogen atoms were included in the structure factor calculations in their expected positions on the basis of idealized bonding geometry but were not refined by least-squares. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

$^+$ Crystal data for 1: C$_{30}$H$_{30}$N$_2$O$_2$P$_2$W, space group $\overline{P}I$, $a = 10.688(3)$, $b = 11.070(2)$, $c = 12.785(2)$, $A$, $\alpha = 88.26(1)$, $\beta = 81.87(2)$, $\gamma = 74.08(2)^\circ$, $V = 1440.0(5)$ $\AA^3$, $Z = 2$. $D_c = 1.65$ g cm$^{-3}$, $\mu = 4.32$ mm$^{-1}$, observed reflections 4557, 20$_{max}$ = 2.49$^\circ$. The structure was solved by using the heavy atom method, a series of difference Fourier maps and refined by least-squares refinements with $R = 0.028$ and $R_w = 0.025$. Hydrogen atoms were included in the structure factor calculations in their expected positions on the basis of idealized bonding geometry but were not refined by least-squares. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

**Scheme 1** Reagents and conditions: i, Me$_3$NO, Ph$_2$NP, MeOH, 25°C, 4 h; ii, Bu$_3$Li, CS$_2$, Et$_4$NBr, MeCN, 25°C, 1 min; iii, heat, THF, 2 h; iv, RX, CH$_2$Cl$_2$, 25°C, 1 min (R = Me, X = I; R = C$_3$H$_5$, X = Br; R = C$_3$H$_5$, X = Br); v, (pip)$_2$W(CO)$_4$, MeCN, 80°C, 1 h; vi, Bu$_3$Li, Et$_4$NBr, MeCN, 25°C (pip = piperidine).
coordination geometry about the tungsten atom can be described as distorted octahedral. The CS₂ unit is attached to the phosphorus atom through carbon with no bonding interaction between the tungsten metal centre and the sulfur atoms, the W-S(1) and W-S(2) distances are 4.056(2) and 4.946(2) Å, respectively. Obviously, 1 was formed by a deprotonation step followed by a nucleophilic attack at the carbon atom of CS₂. In the reaction of W(CO)₆(NH₂C₂H₄)₀₂ with Bu₃Li and CS₂, the CS₂ insertion into the W-N bond gave [W(CO)₄(S₂CNH₂C₂H₄)]Et₄N 2a. The insertion of CS₂ into the Pt-F bond of [Pt(PPh₃₂F)]HF₂ gave [Pt(S₂CF)(PPh₂CMe₂)₂], where the dithiofluoromate ligand coordinates to Pt through two sulfur atoms. 11 Lack of Jₚ-H coupling of this resonance indicates phosphorus coordination.

The reaction of 1 with MeI in CH₂Cl₂ gave a neutral complex W(CO)₄[PPh₂(CS₂CH₃)] 4a in 80% yield. The alkylation takes place at the sulfur atom. In the ¹³C NMR spectrum of 4a, a singlet at δ 21.86 is attributed to the Me of the -CS₂Me group. 11 Contrasts with the observation of a doublet resonance (Jₚ-C 14.7 Hz)12 for the methyl group of the compound [W(η-C₅H₅)(CS₂C(CH₃)₂)] to yield the known dithiocarbamate complex [W(CO)₄(η²-S₂CNCSH₁₀)]Et₄N 5a and the starting material W(CO)₄(PPh₂H) 5b.

We thank the National Science Council of Taiwan, the Republic of China for support.

References

9. A yellow dimeric phosphido complex, [W(CO)₄(PPh₂)], 2, was also isolated in 15% yield, R. L. Keiter and M. J. Madigan, Organometallics, 1982, I, 409.