# Platinum–Manganese and –Rhenium Complexes with Bridging Thiocarbonyl Ligands; Crystal Structure of $[MnPt(\mu\text{-}CS)(CO)_2(PMePh_2)_2(\eta\text{-}C_5H_5)]$

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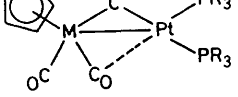
*Summary* The dynamic complexes $[MPt(\mu\text{-}CS)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$ (M = Mn, $PR_3$ = $PMe_2Ph$ or $PMePh_2$; M = Re, $PR_3$ = $PMe_2Ph$) have been prepared by allowing the compounds $[M(CO)_2(CS)(\eta\text{-}C_5H_5)]$ to react with the species $[Pt(C_2H_4)(PR_3)_2]$, and an *X*-ray diffraction study on $[MnPt(\mu\text{-}CS)(CO)_2(PMePh_2)_2(\eta\text{-}C_5H_5)]$ has confirmed the presence of the bridging thiocarbonyl ligand and revealed a strongly semi-bridging CO group.

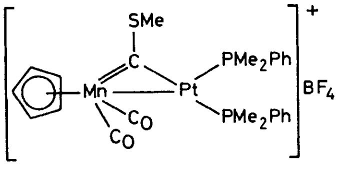
WE have recently shown that complexes with heteronuclear metal–metal bonds and bridging alkylidene or alkylidyne ligands are readily obtained by allowing low-valent transition metal compounds to react with mononuclear carbene or carbyne complexes.[1] It was thus conceivable that nucleophilic complexes of the later transition metals would add to other carbon–metal bonds which are both multiple in character and dipolar in nature, thereby affording a variety of metal–metal-bonded compounds with bridging carbon atoms. There is spectroscopic evidence that the soft CS group can undergo substantial charge fluctuations when bonded to a metal,[2] and nucleophilic attack has been observed at the ligated carbon atoms in certain reactions of metal thiocarbonyls.[3] Hence a study of reactions of Pt(0) compounds with metal–CS bonds appeared to provide a promising route to bridged thiocarbonyl complexes.†

Addition of 1 equiv. of the compounds $[Pt(C_2H_4)(PR_3)_2]$ ($PR_3$ = $PMe_2Ph$ or $PMePh_2$) to the species $[M(CO)_2(CS)(\eta\text{-}C_5H_5)]$ (M = Mn or Re)[4] in light petroleum affords the yellow dimetalla-complexes (**1**) in 60—80% yield. A single-crystal *X*-ray diffraction study was undertaken on complex (**1b**).



(1)

| | M | $PR_3$ |
|---|---|---|
| **a**; | Mn | $PMe_2Ph$ |
| **b**; | Mn | $PMePh_2$ |
| **c**; | Re | $PMe_2Ph$ |



(2)

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† In the carbene or carbyne metal complexes employed in ref. 1 the metal-bonded carbon atoms are electrophilic in character so that attack by $Pt^0$ on these centres is plausible. However, in thiocarbonyl metal complexes the carbon atoms are considered to be electron-rich with respect to the metal (ref. 3) so that reactions with $PtL_2$ species might occur initially at the metal centres, followed by ring closure of the dipolar intermediate. Alternatively, reactions between $d^{10}$ $PtL_2$ species and carbon–metal bonds of multiple character may be frontier-orbital controlled rather than charge controlled (D. L. Lichtenberger and R. F. Fenske, *Inorg. Chem.*, 1976, **15**, 2015).

*Crystal data:* $C_{34}H_{31}MnO_2P_2PtS$, $M = 815{\cdot}7$, monoclinic, space group $P2_1/c$, $a = 16{\cdot}655(4)$, $b = 9{\cdot}684(3)$, $c = 21{\cdot}409(5)$ Å, $\beta = 114{\cdot}57(2)^\circ$, $U = 3\,140{\cdot}2$ Å$^3$, $Z = 4$, $D_c = 1{\cdot}66$ g cm$^{-3}$, $F(000) = 1\,600$, $\mu(\text{Mo-}K_\alpha) = 50{\cdot}8$ cm$^{-1}$. Current $R$ 0·043 ($R'$ 0·043) for 4 358 reflections [295 K, $2\theta \leqslant 50^\circ$, $F \geqslant 5\sigma(F_0)$, Syntex $P2_1$ diffractometer, Mo-$K_\alpha$ $X$-radiation (graphite monochromator), $\bar{\lambda} = 0{\cdot}710\,69$ Å].

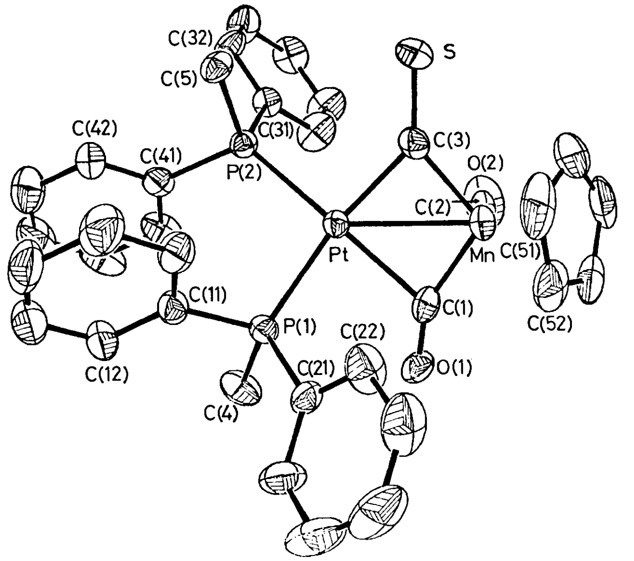

FIGURE. Molecular structure of $[MnPt(\mu\text{-}CS)(CO)_2(PMePh_2)_2(\eta\text{-}C_5H_5)]$. Important internuclear separations and angles include: Mn–Pt 2·641(1), Mn–C(3) 1·878(8), Pt–C(3) 2·015(8), C(3)–S 1·618(8), Mn–C(1) 1·798(8), Pt–C(1) 2·220(9), Pt–P(1) 2·335(2), Pt–P(2) 2·308(2) Å; Mn·C(1)·O(1) 154·0(8), Mn·C(2)·O(2) 173·3(8), Mn·C(3)·S 139·5(5), Pt·C(3)·S 134·8(5), and Pt·C(3)·Mn 85·3(3)°.

The Mn–Pt bond is bridged by the thiocarbonyl ligand (Figure), reflecting the greater tendency of CS compared with CO to occupy a bridging position between metal centres.[5] Nevertheless, one carbonyl ligand C(1)–O(1) [∠ Mn·C(1)·O(1) 154·0(8)°] is markedly semi-bridging,[6] thus accounting for the appearance in the i.r. spectrum of **(1b)**‡ of a CO band at 1 809 cm$^{-1}$.§

Examination of the n.m.r. spectra of the complexes revealed that the CO and CS ligands undergo bridge–terminal site exchange at room temperature. This process ceases at *ca.* −60 °C. At ambient temperatures the $^1$H and $^{31}$P{$^1$H-decoupled} n.m.r. spectra of **(1a)** {in $CD_2Cl_2$, $^1$H, $\tau$ 2·73 (br, 10 H, $C_6H_5$), 5·46 (s, 5 H, $C_5H_5$), and 8·4 [d, 12 H, MeP, $J$(PH) 10, $J$(PtH) 29 Hz]; $^{31}$P, $\delta$ (to high frequency of $H_3PO_4$, p.p.m.), 3·74 [s, $J$(PtP) 3 465 Hz]} showed only one signal for the $PMePh_2$ ligands, but at −60 °C limiting spectra were measured {$^1$H, $\tau$ 2·73 (br, 10 H, $C_6H_5$), 5·40 (s, 5 H, $C_5H_5$), 8·22 [d, 6 H, MeP, $J$(PH) 11, $J$(PtH) 42 Hz], and 8·52 [d, 6 H, MeP, $J$(PH) 9, $J$(PtH) 21 Hz]; $^{31}$P, $\delta$ (p.p.m.) 12·03 [d, $J$(PP) 16, $J$(PtP) 4 213 Hz] and −2·19 [d, $J$(PP) 16, $J$(PtP) 2 647 Hz]}.¶ From the coalescence temperature of the variable-temperature $^{31}$P spectra of **(1a)** the activation energy ($\Delta G^\ddagger$) for bridge–terminal site exchange of the CS ligand was estimated as 12 ± 1 kcal mol$^{-1}$ (1 cal = 4·184 J).

The $^{13}$C{$^1$H-decoupled} n.m.r. spectra were also informative,** showing that the two CO groups continue to exchange after dynamic behaviour of the CS ligand has ceased. Moreover, the $^{13}$C n.m.r. resonances for the CS ligands are more deshielded in the complexes **(1a)**—**(1c)** than in the precursors $[M(CS)(CO)_2(\eta\text{-}C_5H_5)]$ [for M = Mn, $\delta$ (p.p.m.) for the terminal *C*S group is 335,[7] whereas for **(1a)**, $\delta$ (p.p.m.) for $\mu$-*C*S is 386·5]. A similar increase in deshielding is observed for the contact carbon of the carbyne ligand in the complexes $[MPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ (M = Mn or Re) compared with the resonances in the cationic species $[M{\equiv}C(C_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]^+$.[8]

Reaction of **(1a)** with $Me_3OBF_4$ in dichloromethane afforded the red salt **(2)** {$\nu_{CO}$ ($CH_2Cl_2$) 1 979s and 1 857s cm$^{-1}$; n.m.r. ($CH_2Cl_2$–$CD_2Cl_2$, room temperature), $^{31}$P{$^1$H-decoupled}, $\delta$ (p.p.m.) 2·82 [d, $J$(PP) 11, $J$(PPt) 3 917 Hz] and −7·65 [d, $J$(PP) 11, $J$(PPt) 2 631 Hz], $^{13}$C{$^1$H-decoupled}, $\delta$ (p.p.m.) 384·3 [d, $\mu$-*C*SMe, $J$(PC) 72, $J$(PtC) 812 Hz], 223·7 (2 × CO), 134·5 [d, C(1) of $C_6H_5$, $J$(PC) 24 Hz], 133·5 [d, C(1) of $C_6H_5$, $J$(PC) 21 Hz], 130·6, 130·3, 130·1, 128·5, 120·3 ($C_6H_5$), 86·5 ($\eta$-$C_5H_5$), 32·5 (SMe), 16·3 [d, MeP, $J$(PC) 34 Hz], and 14·5 [d, MeP, $J$(PC) 31 Hz]}.

Although **(2)** is formulated as a bridged thiocarbyne complex, further electron delocalization may occur *via* C–S $\pi$-bonding.[9] Moreover, the appearance in the i.r. spectrum of **(2)** of a band at as low a frequency as 1 857 cm$^{-1}$ may

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‡ $\nu_{CO}$ ($CH_2Cl_2$) for **(1a)** 1 993s and 1 829m, for **(1b)** 1 945s and 1 809m, and for **(1c)** 1 931s and 1 845m cm$^{-1}$.

§ 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.

¶ Similar data were obtained from the n.m.r. spectra of the other complexes: **(1b)**, $^{31}$P n.m.r. {$^1$H-decoupled, $CD_2Cl_2$–$CH_2Cl_2$, −70 °C}, $\delta$ (p.p.m.) 25·2 [d, $J$(PP) 24, $J$(PtP) 4 404 Hz] and 7·4 [d, $J$(PP) 24, $J$(PtP) 2 776 Hz]; **(1c)**, $^1$H n.m.r. ($CD_2Cl_2$, −70 °C), $\tau$ 2·78 (m,br, 10 H, $C_6H_5$), 4·82 (s, 5 H, $C_5H_5$), 8·20 [d, 6 H, MeP, $J$(PH) 10, $J$(PtH) 45 Hz], and 8·50 [d, 6 H, MeP, $J$(PH) 8, $J$(PtH) 20 Hz]; $^{31}$P{$^1$H-decoupled, $CD_2Cl_2$–$CH_2Cl_2$, −70 °C}, $\delta$ (p.p.m.) 10·6 [d, $J$(PP) 22, $J$(PtP) 4 558 Hz] and −3·2 [d, $J$(PP) 22, $J$(PtP) 2 512 Hz].

** $^{13}$C{$^1$H-decoupled} N.m.r. data ($CD_2Cl_2$ solution): **(1a)** (at −50 °C), $\delta$ (p.p.m.) 386·5 [d, $\mu$-*C*S, $J$(PC) 71 Hz], 233·7 [d, 2 × CO, $J$(PC) 4, $J$(PtC) 77 Hz], 138 [m, C(1) of $C_6H_5$], 130·0, 129·6, 129·1, 128·0, 127·7 ($C_6H_5$), 88·0 ($C_5H_5$), 14·1 [d, MeP, $J$(PC) 24, $J$(PtC) 31 Hz], and 10·5 [d, MeP, $J$(PC) 34, $J$(PtC) 49 Hz]; **(1c)** (at −70 °C), $\delta$ (p.p.m.) 353·4 [d, $\mu$-*C*S, $J$(PC) 70, $J$(PtC) 806 Hz], 205 (br, 2 × CO), 138·0 [m, C(1) of $C_6H_5$], 129·3, 129·2, 128·7, 128·5, 127·4 ($C_6H_5$), 87·9 ($C_5H_5$), 13·8 [d, MeP, $J$(PC) 19 Hz], and 10·1 [d, MeP $J$(PC) 34, $J$(PtC) 49 Hz].

indicate a mechanism for further charge transfer within the cation *via* CO-bridging to Pt of the type found in [PtW($\mu$-$CC_6H_4Me$-4)$(CO)_2(PMe_2Ph)_2(\eta$-$C_5H_5)$].[1]

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