Formation of Novel Chelating Phosphine Ligands *via* the Reaction of $[\mathrm{W{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)}]$ with the Bidentate Phosphine $\mathrm{C_6H_4(PH_2)_2\text{-}1,2}$; *X*-Ray Crystal Structures of the Complexes $[\mathrm{W\{\sigma,\eta^3\text{-}C_6H_4(PH_2)(PC\{OH\}CH\{C_6H_4Me\text{-}4\})\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)}]$, $[\mathrm{WI\{C_6H_4(PH_2)(P\{Me\}C\{O\}CH_2\{C_6H_4Me\text{-}4\})\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)}]\cdot(1/2\mathrm{C_4H_8O})$, and $[\mathrm{WCo_3(\mu_3\text{-}CR)\{\mu\text{-}C_6H_4(PH_2)(PC\{OH\}CH\{C_6H_4Me\text{-}4\})\text{-}1,2\}(CO)_9(\eta\text{-}C_5H_5)}]$ (R = H or Me)

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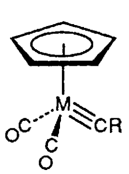
Treatment of the mononuclear alkylidyne complex $[\mathrm{W{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)}]$ with one equivalent of the bidentate phosphine $\mathrm{C_6H_4(PH_2)_2\text{-}1,2}$ affords the metalla-phosphine complex $[\mathrm{W\{\sigma,\eta^3\text{-}C_6H_4(PH_2)(PC\{OH\}CH\{C_6H_4Me\text{-}4\})\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)}]$ which has an unused lone pair of electrons on the central phosphorus atom of the chelate ring and which undergoes *P*-methylation and, like a conventional $\mathrm{PR_3}$ ligand, will substitute CO ligands in transition metal complexes; the structures of the complexes $[\mathrm{W\{\sigma,\eta^3\text{-}C_6H_4(PH_2)(PC\{OH\}CH\{C_6H_4Me\text{-}4\})\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)}]$, $[\mathrm{WI\{C_6H_4(PH_2)(P\{Me\}C\{O\}CH_2\{C_6H_4Me\text{-}4\})\text{-}1,2\}(CO)(\eta\text{-}C_5H_5)}]\cdot(1/2\mathrm{C_4H_8O})$, and $[\mathrm{WCo_3(\mu_3\text{-}CR)\{\mu\text{-}C_6H_4(PH_2)(PC\{OH\}CH\{C_6H_4Me\text{-}4\})\text{-}1,2\}(CO)_9(\eta\text{-}C_5H_5)}]$ (R = H or Me) have been determined by single crystal *X*-ray diffraction studies.

The alkylidyne complexes $[\mathrm{M{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)}]$ [M = W (**1a**), M = Mo (**1b**)] react with a variety of phosphine ligands ($\mathrm{PR_3}$) to give the η^2-ketenyl derivatives (**2**),[1,2] which in the case of the Mo complexes (**2b**) readily decarbonylate, affording the phosphine substituted alkylidyne complexes (**3**).[3] Moreover, the related reaction of (**1a**) with the bidentate phosphine[4] *rac*-$\mathrm{C_6H_4(PMePh)_2\text{-}1,2}$ is remarkably stereospecific and gives only one diastereoisomer of the σ-ketenyl complex (**4**).[5] We now report the novel product obtained from the reaction between (**1a**) and the bidentate primary phosphine[6] $\mathrm{C_6H_4(PH_2)_2\text{-}1,2}$.

Treatment of the complex $[\mathrm{W{\equiv}CC_6H_4Me\text{-}4(CO)_2(\eta\text{-}C_5H_5)}]$

(1a) with one equivalent of the bidentate phosphine $C_6H_4(PH_2)_2$-1,2 (Et_2O, reflux) leads to near-quantitative precipitation of the bright orange complex [W{σ,η^3-$C_6H_4(PH_2)(PC\{OH\}CH\{C_6H_4Me$-4})-1,2}(CO)(η-$C_5H_5$)] **(5)** (Scheme 1). The structure of **(5)** was established by a single crystal *X*-ray diffraction study† which shows that the central P(2) atom of the chelate chain is part of a phospha-allyl moiety PC(OH)CH(C_6H_4Me-4). Formation of **(5)** presumably proceeds *via* an unstable intermediate analogous to the complex **(4)**. Stereospecific migration of the PH_2 hydrogen atoms to the ketenyl ligand, with concurrent P–C bond formation, would give **(5)**. Solution spectroscopic data for **(5)**‡ are consistent with the solid-state structure and the chelating phosphorus atom P(2) is characterised by an unusually small *J*(WP) value of 60 Hz [*cf.* WPH_2, *J*(WP) 308 Hz].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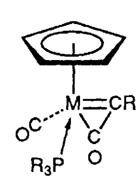
(1a) W
(1b) Mo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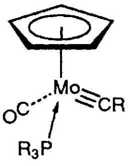
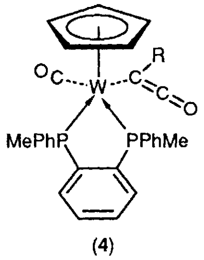
(2b) Mo


(3)


(4)

R = C_6H_4Me-4

The central P(2) atom in **(5)** formally has an unused lone pair of electrons, and the complex as a whole behaves as a novel metalla-substituted phosphine ligand. Thus, methylation (Me_3OBF_4 or MeI; CH_2Cl_2; 20 °C) of **(5)** occurs at P(2) affording the enol-phosphine cations [W{σ^2,η^2-$C_6H_4(PH_2)(P\{Me\}C\{OH\}{=}CH\{C_6H_4Me$-4})-1,2}(CO)(η-$C_5H_5$)]$^+$ **(6)** and **(7)**, respectively. Compound **(6)** is stable in CH_2Cl_2, but the more strongly co-ordinating solvent MeCN slowly (1 day; 20 °C) displaces co-ordination of the enol moiety, affording the MeCN cation [W{σ^2-$C_6H_4(PH_2)(P\{Me\}C\{OH\}{=}CH\{C_6H_4Me$-4})-1,2}(MeCN)(CO)(η-$C_5H_5$)]$^+$ **(8)**. The complex **(8)** subsequently undergoes very slow (10 day; 20 °C; MeCN) enol–keto tautomerisation, affording the ketone derivative [W{σ^2-$C_6H_4(PH_2)(P\{Me\}C\{O\}CH_2\{C_6H_4Me$-4})-1,2}(MeCN)-(CO)-(η-$C_5H_5$)]$^+$ **(9)**.

The complex **(7)** is stable in the solid state and almost insoluble in CH_2Cl_2. On stirring in CH_2Cl_2 the complex dissolves and isomerises to the co-ordinated iodide complex [WI{$C_6H_4(PH_2)(P\{Me\}C\{O\}CH_2\{C_6H_4Me$-4})-1,2}(CO)-(η-$C_5H_5$)] **(10)**. The structure of the complex **(10)** was established by a single-crystal *X*-ray diffraction study.† The isomerisation of **(7)** to **(10)** may well proceed *via* an enol

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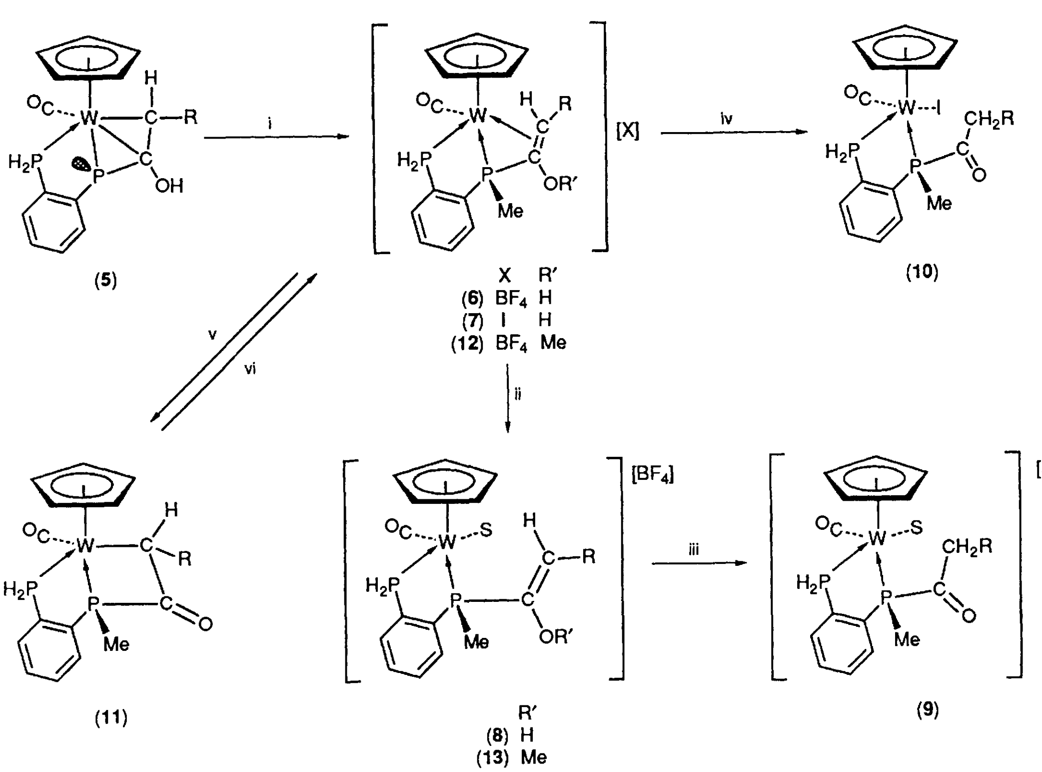
† *Crystal data* for **(5)**: $C_{21}H_{20}O_2P_2W$, M = 550.2, triclinic, space group $P\bar{1}$, a = 9.182(3), b = 10.279(4), c = 12.058(5) Å, α = 108.35(3), β = 110.96(3), γ = 73.53(3)°, U = 989.8(6) Å^3, Z = 2, D_c = 1.85 g cm^{-3}, $F(000)$ = 532, μ(Mo-K_α) = 61.3 cm^{-1}, R = 0.022 (R_w = 0.024) for 3216 unique absorption-corrected intensities [298 K, WycKoff ω-scans, 2θ ⩽ 50°, $F \geqslant 5\sigma(F)$, Mo-K_α ($\bar{\lambda}$ = 0.71069 Å)]. For **(10)**·(1/2C_4H_8O): $C_{22}H_{23}IO_2P_2W$·(1/2C_4H_8O), M = 728.2, triclinic, space group $P\bar{1}$, a = 8.892(3), b = 10.232(3), c = 14.315(6) Å, α = 77.60(3), β = 75.31(3), γ = 89.68(3)°, U = 1228.8(8) Å^3, Z = 2, D_c = 1.97 g cm^{-3}, $F(000)$ = 696, μ(Mo-K_α) = 61.9 cm^{-1}, R = 0.024 (R_w = 0.026) for 3982 unique absorption-corrected intensities [298 K, WycKoff ω-scans, 2θ ⩽ 50°, $F \geqslant 5\sigma(F)$]. For **(15a)**: $C_{30}H_{21}Co_3O_{10}P_2W$, M = 964.0, triclinic, space group $P\bar{1}$, a = 9.897(3), b = 10.400(2), c = 16.196(3) Å, α = 95.27(2), β = 101.71(2), γ = 93.62(2)°, U = 1619.6(7) Å^3, Z = 2, D_c = 1.98 g cm^{-3}, $F(000)$ = 932, μ(Mo-K_α) = 52.8 cm^{-1}, R = 0.029 (R_w = 0.032) for 4729 unique absorption-corrected intensities [298 K, WycKoff ω-scans, 2θ ⩽ 50°, $F \geqslant 5\sigma(F)$]. For **(16)**: $C_{31}H_{23}Co_3O_{10}P_2W$, M = 978.1, triclinic, space group $P\bar{1}$, a = 8.477(2), b = 12.886(2), c = 15.601(3) Å, α = 98.21(1), β = 97.94(2), γ = 92.92(1)°, U = 1666.1(5) Å^3, Z = 2, D_c = 1.95 g cm^{-3}, $F(000)$ = 948, μ(Mo-K_α) = 51.3 cm^{-1}, R = 0.034 (R_w = 0.035) for 5090 unique absorption-corrected intensities [298 K, WycKoff ω-scans, 2θ ⩽ 50°, $F \geqslant 5\sigma(F)$].

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.

‡ All compounds have been fully characterised by elemental analysis and spectroscopy. Only selected spectroscopic data are given. Unless otherwise noted, IR spectra were measured in CH_2Cl_2 and NMR spectra in CD_2Cl_2 or CD_3CN. Coupling constants in Hz, chemical shifts in ppm relative to $SiMe_4$ [^{1}H, ^{13}C-{^{1}H}] or external H_3PO_4 [^{31}P-{^{1}H} or ^{31}P]. Compound **(5)**: orange crystals, $\nu_{max.}$ (CO) 1862s cm^{-1}; NMR; ^{1}H, δ 3.72 [dd, 1 H, C*H*R, *J*(PH) 12, 2]; ^{31}P, δ −52.6 [PC(OH), *J*(WP) 60] and −28.3 [dd, PH_2, *J*(HP) 337, 359, *J*(WP) 308]; ^{13}C-{^{1}H}, δ 233.1 [d, WCO, *J*(PC) 19] and 32.5 [d, *C*HR, *J*(PC) 37]. Compound **(6)**: yellow crystals, $\nu_{max.}$ (Nujol) (CO) 1932s cm^{-1}; NMR; ^{1}H, δ 4.55 [dd, 1 H, C*H*R, *J*(PH) 3, 8]; ^{31}P, δ −37.5 [ddd, PH_2, *J*(HP) 379, 403, *J*(PP) 15, *J*(WP) 286] and −11.9 [d, P(Me)C(OH), *J*(PP) 15]; ^{13}C-{^{1}H}, δ 224.5 [d, WCO, *J*(PC) 12] and 35.3 [d, *C*HR, *J*(PC) 24]. Compound **(7)**: yellow crystals, $\nu_{max.}$ (Nujol) (CO) 1939s cm^{-1}. Compound **(8)**: yellow oil, $\nu_{max.}$ (CO) 1888s and $\nu_{max.}$ (C=C) 1604w cm^{-1}; NMR; ^{1}H, δ 6.06 [d, 1 H, C*H*R, *J*(PH) 8], 2.96 (s, 1 H, OH); ^{31}P, δ −17.7 [ddd, PH_2, *J*(HP) 362, 398, *J*(PP) 22, *J*(WP) 234], 51.6 [d, P(Me)C(OH), *J*(PP) 22]; ^{13}C-{^{1}H}, δ 235.7 [d, WCO, *J*(PC) 24] and 114.1 [d, *C*HR, *J*(PC) 14]. Compound **(9)**: yellow crystals, $\nu_{max.}$ (CO) 1888s and $\nu_{max.}$ (C=O) 1684m cm^{-1}; NMR; ^{1}H, δ 3.64 [d, 1 H, C(O)C*H*$_2$R, *J*(HH) 16] and 3.31 [d, 1 H, C(O)C*H*$_2$R, *J*(HH) 16]; ^{31}P, δ −19.4 [ddd, PH_2, *J*(HP) 385, 365, *J*(PP) 22] and 58.0 [d, P(Me)C(O), *J*(PP) 22]; ^{13}C-{^{1}H}, δ 234.1 [d, WCO, *J*(PC) 22], 217.2 [d, P(Me)*C*(O), *J*(PC) 10], and 46.0 [d, C(O)*C*H$_2$R, *J*(PC) 42]. Compound **(10)**: dark red crystals, $\nu_{max.}$ (CO) 1862vs and $\nu_{max.}$ (C=O) 1692m cm^{-1}; NMR; ^{1}H, δ 3.94 [d, 1 H, C(O)C*H*$_2$R, *J*(HH) 16] and 3.30 [d, 1 H, C(O)C*H*$_2$R, *J*(HH) 16]; ^{31}P, δ −12.3 [ddd, PH_2, *J*(PH) 385, 343, *J*(PP) 22, *J*(WP) 264] and 46.1 [d, P(Me)C(O), *J*(PP) 22, *J*(WP) 316]; ^{13}C-{^{1}H}, δ 229.4 [d, WCO, *J*(PC) 22], 218.6 [d, P(Me)*C*(O), *J*(PC) 17], and 44.7 [d, C(O)*C*H$_2$R, *J*(PC) 43]. Compound **(11)**: yellow crystals, $\nu_{max.}$ (CO) 1854vs and $\nu_{max.}$ (C=O) 1598s cm^{-1}; NMR; ^{1}H, δ 4.97 (s, 1 H, C*H*R); ^{31}P, δ −26.0 [ddd, PH_2, *J*(HP) 381, 323, *J*(PP) 22, *J*(WP) 286] and 57.0 [d, P(Me)C(O), *J*(PP) 22]; ^{13}C-{^{1}H}, δ 232.3 [d, WCO, *J*(PC) 20], 162.3 [d, P(Me)*C*(O), *J*(PC) 12], and 38.1 [d, C(O)*C*HR, *J*(PC) 56]. Compound **(12)**: yellow crystals, $\nu_{max.}$ (CO) 1976s cm^{-1}; NMR; ^{1}H, δ 4.19 [d, 1 H, C*H*R, *J*(PH) 9] and 3.26 (s, 3 H, OMe); ^{31}P, δ −41.9 [dd, PH_2, *J*(HP) 457, 457, *J*(WP) 264] and −1.7 [P(Me)C(OMe)]. Compound **(13)**: yellow crystals, $\nu_{max.}$ (CO) 1884s and $\nu_{max.}$ (C=C) 1682w cm^{-1}; NMR; ^{1}H, δ 6.39 [d, 1 H, C*H*R, *J*(PH) 7] and 3.23 (s, 3 H, OMe); ^{31}P, δ −19.2 [ddd, PH_2, *J*(HP) 395, 385, *J*(PP) 29] and 43.8 [d, P(Me)C(OMe), *J*(PP) 29]. Compound **(15a)**: dark green crystals and solutions, $\nu_{max.}$ (CO) 2072s, 2029s, 2015s,sh, and 1901m cm^{-1}; NMR; ^{1}H, δ 11.86 (s, 1 H, μ_3-CH), 4.54 [d, 1 H, C*H*R, *J*(PH) 12], and 2.56 (s, 1 H, OH); ^{31}P, δ −18.4 (br., CoP) and −30.1 [ddd, PH_2, *J*(HP) 357, 371, *J*(PP) 14, *J*(WP) 293]. Compound **(15b/16)**: dark green solutions, red crystals, $\nu_{max.}$ (CO) (CH_2Cl_2) 2068s, 2024s, 2009s, sh, and 1894m cm^{-1}; NMR; ^{1}H, δ 4.64 [dd, 1 H, C*H*R, *J*(PH) 12, 2] and 2.63 [d, 1 H, OH, *J*(PH) 3]; ^{31}P, δ −19.2 (br., CoP) and −29.9 [ddd, PH_2, *J*(PH) 362, 373, *J*(PP) 14, *J*(WP) 294].



R = C_6H_4Me-4, S = MeCN

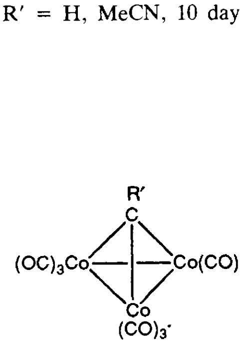
Scheme 1. *Reagents and conditions:* i, Me_3OBF_4 or MeI; ii, MeCN; iii, R' = H, MeCN, 10 days; iv CH_2Cl_2, 20 °C; v, Et_3N, MeCN; vi, Me_3OBF_4, CH_2Cl_2.

intermediate analogous to (**8**), which undergoes a rapid I^- catalysed tautomerisation to the keto-isomer (**10**).

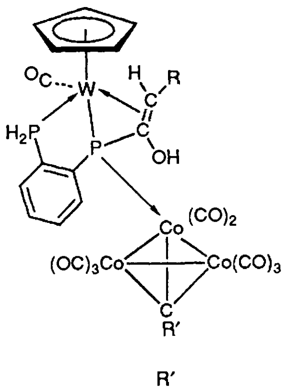
Deprotonation (Et_3N, MeCN) of the hydroxy ligand in (**6**) affords the neutral complex [W{σ^3-$C_6H_4(PH_2)$(P{Me}C-{O}CH{C_6H_4Me-4})-1,2}(CO)(η-C_5H_5)] (**11**). The IR spectrum‡ of (**11**) has a band at 1598 cm^{-1} which may be assigned to the C=O group of the metalla-phosphacyclobutanone ring system. The complex (**11**) undergoes facile *O*-methylation (Me_3OBF_4, CH_2Cl_2) giving the complex [W{σ^2,η^2-$C_6H_4(PH_2)$(P{Me}C{OMe}=CH{C_6H_4Me-4})-1,2}(CO)(η-C_5H_5)][BF_4] (**12**), a methoxy derivative of the hydroxy precursor (**6**). The co-ordination of the methoxyvinyl group in (**12**) is slowly (3 days; 20 °C) displaced in MeCN, affording the solvated cation [W{σ^2-$C_6H_4(PH_2)$(P{Me}C{OMe}=CH-{C_6H_4Me-4})-1,2}(MeCN)(CO)(η-C_5H_5)]$^+$ (**13**). The presence of the methoxy group in the latter complex prevents the enol–keto tautomerisation which occurs for the hydroxy analogue (**8**).

The metalla-phosphine character of (**5**) is further emphasised by its ability to carry out simple carbonyl substitution reactions in transition metal clusters. Thus, treatment of the tri-cobalt alkylidyne clusters [$Co_3(\mu_3$-CR)$(CO)_9$] [R = H (**14a**) or Me (**14b**)]^7 with one equivalent of (**5**) (CH_2Cl_2–Et_2O, 1:2; 20 °C) gives deep green solutions of the complexes [$WCo_3(\mu_3$-CR){μ-$C_6H_4(PH_2)$(PC{OH}CH{C_6H_4Me-4})-1,2}-$(CO)_9(\eta$-$C_5H_5)$] [R = H (**15a**) or Me (**15b**)]. Solution spectroscopic data‡ for (**15a,b**) are consistent with the structure† established for the dark green crystals obtained for the methylidyne complex (**15a**). The structure of (**15a**) confirms that the complex (**5**) has formally replaced an equatorial CO ligand in the parent Co_3 complex (**14a**).

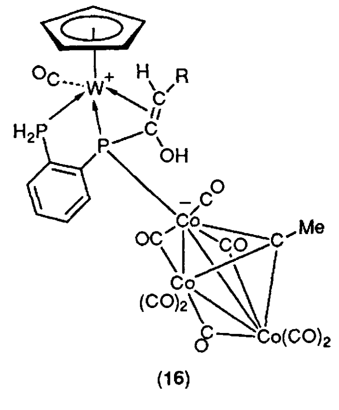
In marked contrast, deep green solutions of the ethylidyne complex (**15b**) give transparent red crystals and a single crystal *X*-ray diffraction study† reveals that it adopts the solid-state



R'
(**14a**) H
(**14b**) Me



R'
(**15a**) H
(**15b**) Me



(**16**)

R = C_6H_4Me-4

structure (**16**), in which each edge of the triangle of cobalt atoms is bridged by a carbonyl ligand, with the complex (**5**) occupying an axial co-ordination site. All previous structure determinations on the extensive range of neutral complexes with simple $Co_3(\mu\text{-}CR)(CO)_{9-n}(L)_n$ (L = phosphine or CO) cores have terminal CO ligands as found for (**15a**). It is significant that the solid-state structure of the complex $[Li][Co_3(\mu\text{-}CO)_3(CO)_6]$ has a carbonyl-bridged Co_3 core similar to that found in (**16**).[8] The anionic character of the latter complex suggests that charge transfer from W to Co, as shown in (**16**), might augment crystal-packing forces in stabilising the extremely unusual CO bridged conformation observed in the solid state for this complex.

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