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π-Arene complexes
IX*. Crystal structure of a novel benzoyl bridged heterobimetallic complex, [*cis*-$(CO)_4\{(MeO)_3P\}Mn\{\mu\text{-}\eta^1{:}\eta^6\text{-}C_6H_5C(O)\}Cr(CO)_3$]

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Abstract

The bimetallic complex [*cis*-$(CO)_4\{(MeO)_3P\}Mn(\mu\text{-}(\eta^1{:}\eta^6\text{-}C(O)C_6H_5))Cr(CO)_3$] (**1**) was obtained by the reaction of [$(\eta^6\text{-}C_6H_5Li)Cr(CO)_3$] with $Mn(CO)_5Br$ in the presence of one equivalent of $P(OMe)_3$ at low temperature. The structure of **1**, determined by single crystal X-ray diffraction methods, shows the coordination around the manganese atom to be approximately octahedral, with the manganese moiety displaced from the plane of the η^6-arene ring away from the $Cr(CO)_3$ group. The phosphite ligand is located on the same side of the molecule as the chromium tripodal moiety, and interlocked between carbonyl ligands. Crystals of **1** are triclinic, space group $P\bar{1}$, with $Z=2$ in a unit cell of dimensions $a=8.658(1)$, $b=10.300(1)$, $c=11.891(1)$ Å, $\alpha=90.75(1)$, $\beta=95.29(1)$ and $\gamma=95.16(1)°$. The structure was refined to $R_w=0.029$ for 290 parameters using 5112 observed reflections.

Introduction

Complexes with σ,π arene ligands constitute an area of research of growing interest [2–8]. Investigation of the reactivity of lithiated π-arene complexes of chromium(0) with transition metal substrates which contain halogen ligands, recently enabled us to isolate heterobimetallic compounds with bridging σ,π-bonded benzoyl and σ,π-bonded benzene ligands [1, 9]. Whereas bridging benzene complexes were obtained when one equivalent of triphenylphosphine was added to the reaction mixture of the lithiated arene and [$Mn(CO)_5Br$], the addition of bidentate phosphine and ammine ligands afforded bridging benzoyl products. In the absence of another σ-donor, a carbonyl ligand was incorporated into the final product and a bridging benzoyl ligand resulted.

In the reaction discussed here, which represents a modification of the synthetic procedure published earlier [9], trimethylphosphite was added to a mixture of the lithiated benzene precursor and manganese substrate, whereby a mixture of σ,π-bridged benzene and benzoyl complexes of Cr–Mn was obtained. Of particular interest is the structure and conformation of [*cis*-$(CO)_4\{P(OMe)_3\}Mn\{\mu\text{-}(\eta^1{:}\eta^6\text{-}C(O)C_6H_5)\}Cr(CO)_3$ (**1**).

Experimental

Preparation of [cis-$(CO)_4\{P(OMe)_3\}Mn\{\mu\text{-}(\eta^1{:}\eta^6\text{-}C(O)C_6H_5)\}Cr(CO)_3$] (1)

Small portions of n-butyllithium (1.87 cm^3, 3 mmol of a 1.6 mol/dm^3 solution in hexane) were added to a well-stirred THF/hexane (1/1) solution of $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ (0.64 g, 3 mmol) maintained at −78 °C by a dry ice/acetone bath. Following the dropwise addition, the solution was allowed to warm slowly to −30 °C and stirring was continued for 40 min. The reaction mixture was again cooled (−78 °C) and added to a THF solution (−50 °C) of $Mn(CO)_5Br$ (0.825 g, 3 mmol). After 15 min, $P(OMe)_3$ (0.42 cm^3, 5 mmol) was added in drops to the cooled solution with vigorous stirring. The reaction mixture was stirred for 10 min, removed from the cold bath and stirred at ambient temperature for 30 min before the solvent was removed under reduced pressure. The red–brown crude product was filtered through a plug of silica gel and purified by chromatography on a silica gel column with dichloromethane/hexane (1:1) as eluent. The first yellow fraction collected was unreacted (π-benzene)-tricarbonylchromium and the next fraction afforded an orange product [*cis*-$(CO)_4\{P(OMe)_3\}Mn\{\mu\text{-}(\eta^1{:}\eta^6\text{-}C_6H_5)\}Cr(CO)_3$] (**2**) (0.28 g, 0.55 mmol, 17%) which was characterized by ^1H NMR and IR spectroscopy. The third fraction collected was the main product and yielded [*cis*-$(CO)_4\{P(OMe)_3\}Mn\{\mu\text{-}(\eta^1{:}\eta^6\text{-}C(O)\text{-}$

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*Part VIII is ref. 1.

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$C_6H_5)\}Cr(CO)_3)]$ (**1**) after recrystallization from dichloromethane/hexane mixtures (1.1 g, 2.2 mmol, 69%) m.p. 94–95 °C. *Anal.* Calc. for $CrMnC_{17}H_{14}O_{11}P$: C, 38.3; H, 2.63. Found: C, 39.1; H, 2.71%.

Decarbonylation of [cis-(CO)$_4${P(OMe)$_3$}Mn{μ-(η^1:η^6-C(O)C$_6$H$_5$)Cr(CO)$_3$ (1)

A suspension of **1** (1.06 g, 2 mmol) in hexane was refluxed at 70 °C. The reaction was monitored by the disappearance of the acyl band at 1584 cm^{-1} in the IR spectra measured at 15 min intervals. The conversion was quantitative after 4 h and the yellow powder obtained after removal of the hexane afforded [*cis*-$(CO)_4\{P(OMe)_3\}Mn\{\mu$-$(\eta^1{:}\eta^6$-$C_6H_5)\}Cr(CO)_3]$ (**2**) (0.95 g, 95%).

Crystal structure determination of complex 1

A needle-shaped orange crystal, of approximate dimensions 0.22×0.35×0.48 mm, was used for the X-ray analysis.

TABLE 1. Fractional atomic coordinates (×10^4) and equivalent thermal factors (×10^3 Å^2) for **1**

Atom	x/a	y/b	z/c	U_{eq}[a]
Cr	2638(1)	2648(1)	5765(1)	2(1)
C(1)	4633(3)	2303(2)	5518(2)	44(1)
O(1)	5880(2)	2057(2)	5411(2)	72(1)
C(2)	2121(3)	894(3)	5833(2)	53(1)
O(2)	1770(3)	−212(2)	5880(2)	90(1)
C(3)	3345(3)	2661(3)	7274(2)	52(1)
O(3)	3831(3)	2654(3)	8202(2)	94(1)
C(4)	2810(3)	4584(2)	4975(2)	34(1)
C(5)	2006(3)	4678(2)	5935(2)	40(1)
C(6)	678(3)	3819(2)	6060(2)	41(1)
C(7)	157(3)	2883(2)	5217(2)	38(1)
C(8)	970(2)	2782(2)	4243(2)	32(1)
C(9)	2300(2)	3633(2)	4120(2)	30(1)
C(10)	3269(3)	3606(2)	3104(2)	33(1)
O(4)	4677(2)	3777(2)	3330(1)	50(1)
Mn	2296(1)	3581(1)	1437(1)	30(1)
C(11)	261(3)	3357(2)	1786(2)	36(1)
O(5)	−1022(2)	3230(2)	1923(2)	56(1)
C(12)	2408(3)	5334(3)	1696(2)	45(1)
O(6)	2498(2)	6429(2)	1888(2)	79(1)
C(13)	4348(3)	3726(2)	1035(2)	43(1)
O(7)	5569(2)	3806(2)	778(2)	69(1)
C(14)	1528(3)	3679(2)	−46(2)	43(1)
O(8)	1008(2)	3778(2)	−950(2)	70(1)
P	2396(1)	1409(1)	1359(1)	35(1)
O(9)	1285(2)	679(2)	2172(2)	57(1)
C(15)	1103(4)	−724(3)	2294(3)	86(1)
O(10)	4030(2)	818(2)	1583(2)	56(1)
C(16)	4871(4)	786(3)	2679(3)	82(1)
O(11)	1897(2)	812(2)	131(1)	55(1)
C(17)	2398(4)	−322(3)	−362(3)	88(1)

[a] $U_{eq}=\frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*(\mathbf{a}_i\cdot\mathbf{a}_j)$.

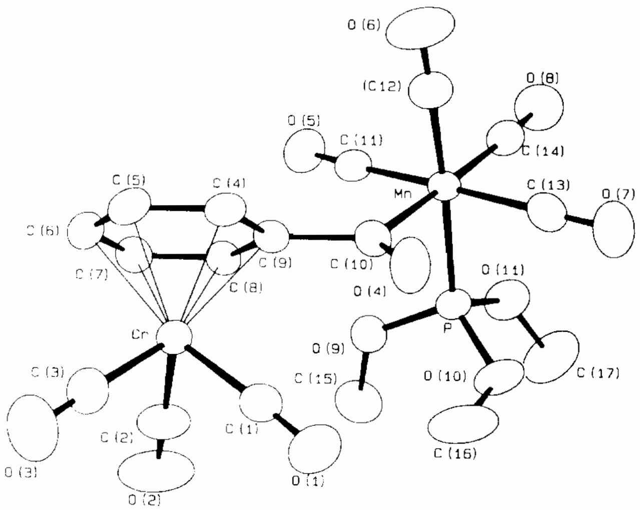


Fig. 1. Perspective view of **1**, showing the atomic numbering scheme used. Hydrogen atoms are not displayed.

Crystal data

$C_{17}H_{14}O_{11}PCrMn$, $M=532.20$, triclinic, space group $P\bar{1}$ (No. 2), $a=8.658(1)$, $b=10.300(1)$, $c=11.891(1)$ Å, $\alpha=90.75(1)$, $\beta=95.29(1)$, $\gamma=95.16(1)$°, $V=1051(1)$ Å^3, $\lambda=0.7107$ Å, $Z=2$, $D_c=1.68$ g cm^{-3}, μ(Mo Kα) = 11.80 cm^{-1}, $F(000)=536.0$.

Data collection and processing

Accurate unit cell parameters were obtained by least-squares methods from the position of 25 centred reflections (all with $\theta>24°$) on an Enraf Nonius CAD4 diffractometer with Mo Kα radiation (graphite monochromator). A total of 6113 unique reflections ($3\leqslant\theta\leqslant30°$) was measured using an $\omega{:}2\theta$ ratio of 3:2 and a scan angle of $0.57+0.35\tan\theta°$. The zone collected is h (0 to 12), k (−14 to 14) and l (−16 to 16). There was no significant crystal decay and intensities were corrected for absorption (max., min., av. correction factors 1.00, 0.929, 0.977), as well as for Lorentz and polarization effects.

Structural analysis and refinement

The structure was solved by Patterson methods [10]. Refinement was by full-matrix least-squares methods [11]. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed in idealized positions with a common isotropic thermal parameter that refined to $U_{iso}=0.101(3)$ Å^2. Convergence was reached at $R=0.034$, $R_w=0.029$ using the weighting scheme $w=[\sigma^2(F_o)+0.00166F_o{}^2]^{-1}$, with the largest shift/e.s.d. less than 0.09. A total of 290 parameters was refined using 5112 reflections with $F>6\sigma(F)$. The maximum and minimum residual electron densities of the final difference map were 0.34 and −0.32 e Å^{-3}. Fractional coordinates of the non-hydrogen atoms are given in Table 1, and the perspective view of the molecule in Fig. 1 was prepared with ORTEP [12], illustrating the crystallographic numbering scheme used. Atomic scattering factors were taken from the literature [13].

Results and discussion

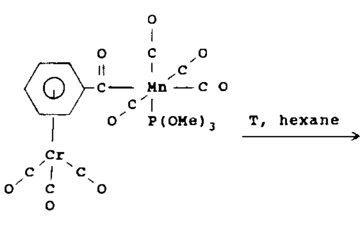
Complex **1** was prepared in high yield by adding trimethylphosphite to a cold (−30 °C) THF/hexane (1/1) solution of $(\eta^6\text{-}C_6H_5Li)Cr(CO)_3$ and $Mn(CO)_5Br$. Experimental observations did not indicate that the phosphite ligand promoted migration of the arene ligand to a carbonyl ligand of the manganese fragment. In fact, **1** was also obtained in a high yield when $P(OMe)_3$ was added before the lithiated precursor. Thus, a mechanism involving the formation of an acyl(tetracarbonyl) intermediate, in this instance, also seems reasonable [14]. In addition, the complex [*cis*-$(CO)_4\{P(OMe)_3\}Mn\{\mu\text{-}(\eta^1{:}\eta^6\text{-}C_6H_5)\}Cr(CO)_3$] (**2**), formed in a low yield and is representative of a σ,π-bridged benzene complex. Complex **1** was converted quantitatively into complex **2** by refluxing the benzoyl precursor in hexane for 4 h (Scheme 1). However, in tetrahydrofuran, complex **2** slowly converts back into **1** and some decomposition of the products occurs. Although complex **2** is thermodynamically less stable than **1**, it is possible to handle both solids under inert atmosphere.

TABLE 2. Selected bond lengths (Å) and valence angles (°) for **1**

Bond lengths			
Cr–C(1)	1.843(2)	Cr–C(2)	1.826(3)
Cr–C(3)	1.841(3)	Cr–C(4)	2.215(2)
Cr–C(5)	2.220(2)	Cr–C(6)	2.219(2)
Cr–C(7)	2.222(2)	Cr–C(8)	2.224(2)
Cr–C(9)	2.224(2)	C(1)–O(1)	1.149(3)
C(2)–O(2)	1.156(3)	C(3)–O(3)	1.144(3)
C(4)–C(5)	1.398(3)	C(4)–C(9)	1.415(3)
C(5)–C(6)	1.407(3)	C(6)–C(7)	1.396(3)
C(7)–C(8)	1.417(3)	C(8)–C(9)	1.403(3)
C(9)–C(10)	1.534(3)	C(10)–O(4)	1.220(2)
C(10)–Mn	2.080(2)	Mn–C(11)	1.842(2)
Mn–C(12)	1.820(3)	Mn–C(13)	1.876(3)
Mn–C(14)	1.834(2)	Mn–P	2.248(1)
C(11)–O(5)	1.133(2)	C(12)–O(6)	1.142(3)
C(13)–O(7)	1.124(3)	C(14)–O(8)	1.135(3)
P–O(9)	1.576(2)	P–O(10)	1.591(2)
P–O(11)	1.584(2)	O(9)–C(15)	1.451(3)
O(10)–C(16)	1.436(3)	O(11)–C(17)	1.420(3)
Bond angles			
Cr–C(1)–O(1)	176.7(2)	Cr–C(2)–O(2)	178.9(3)
Cr–C(3)–O(3)	177.6(2)	C(5)–C(4)–C(9)	120.7(2)
C(4)–C(5)–C(6)	120.0(2)	C(5)–C(6)–C(7)	119.8(2)
C(6)–C(7)–C(8)	120.4(2)	C(7)–C(8)–C(9)	119.8(2)
C(4)–C(9)–C(8)	119.3(2)	C(4)–C(9)–C(10)	116.6(2)
C(8)–C(9)–C(10)	124.1(2)	C(9)–C(10)–O(4)	115.3(2)
C(9)–C(10)–Mn	123.2(1)	O(4)–C(10)–Mn	120.8(2)
Mn–P–O(9)	112.1(1)	Mn–P–O(10)	119.6(1)
O(9)–P–O(10)	106.1(1)	Mn–P–O(11)	112.3(1)
O(9)–P–O(11)	106.6(1)	O(11)–P–O(11)	98.7(1)
P–O(9)–C(15)	124.3(2)	P–O(10)–C(16)	123.6(2)
P–O(11)–C(17)	127.6(2)		

Description of the crystal structure of [cis-$(CO)_4\{P(OMe)_3\}Mn\{\mu\text{-}(\eta^1{:}\eta^6\text{-}C(O)C_6H_5)Cr(CO)_3]$ (1)

The structure of complex **1** is represented in Fig. 1; selected bond distances and angles are given in Table 2. The Cr–CNTR (the calculated centroid of the aromatic ring) distance of 1.719(3) Å, as well as the averaged Cr–CNTR–C(arene) angle of 89.9(1)°, confirm the planar η^6-coordination of the arene ligand. The coordination around the manganese atom is approximately octahedral with the most significant distortion in the C10–Mn–C12 and C12–Mn–C14 angles which are 82.2(1) and 94.1(1)°, respectively. This represents a slight tilt of the C10 and C12 carbonyl groups towards the bridging benzoyl ligand, unlike what is normally found for pentacarbonyl complexes of chromium with one weaker π-acceptor ligand, where the distortion of the equatorial carbonyls is away from the unique ligand [15]. The acyl group approaches coplanarity with the three other carbonyl ligands in the equatorial plane (C10–C11–C14–C13) and torsion angles for O4–C10–Mn–C14 and O4–C10–Mn–C13 of 2.1(2) and 4.7(2)° respectively, were recorded. Conversely, the torsion angle C8–C9–C10–Mn (49.7(3)°) shows a rotation around the C9–C10 bond for the manganese fragment away from the plane of the arene ring, in the direction opposite to the chromium group. There is also a slight enlargement of the C(arene)–C(acyl)–Mn angle (C9–C10–Mn = 123.2(2)°), due to some mild nonbonded interactions between H8 and C11 (2.558 Å), and H8 and O9 (2.345 Å). This aspect is highlighted in an ORTEP drawing in Fig. 2 showing a view parallel to the arene ring, which clearly shows the acyl unit twisted towards the $Cr(CO)_3$ side of the plane of the arene ring (torsion angle C4–C9–C10–O4 = 39.9(3)°). This phenomenon is not nearly as pronounced as previously recorded for a corresponding acyl unit in the complex $[Et_4N][(CO)_4Fe\{\mu\text{-}(\eta^1{:}\eta^6\text{-}o\text{-}C(O)C_6H_4Cl)\}$-



Scheme 1.

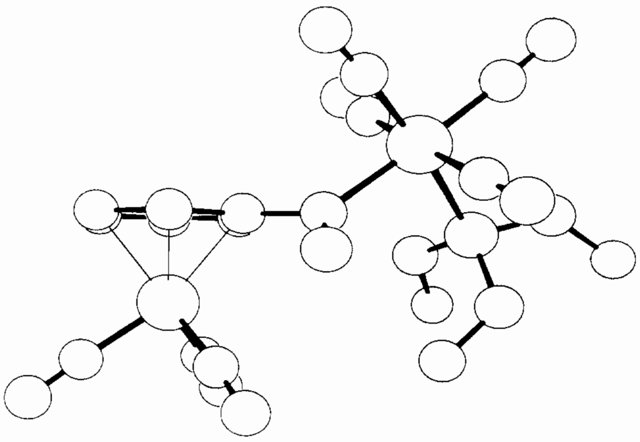


Fig. 2. Perspective view parallel to the arene ring of **1**, showing the twist in the acyl group.

$Cr(CO)_3$] (corresponding torsion angle was 89.0°) [16]. The angle between the plane of the arene ring and the equatorial plane of the manganese ligand defined by C10–C11–C14–C13 is 49.0(6)°.

An ongoing and longstanding controversy exists about whether the C–C bonds are fixed into alternating single and double bonds in π-arenechromium and related complexes [17]. Alternating longer and shorter bond distances are recorded for **1** (C4–C5 = 1.398(3), C5–C6 = 1.407(3), C6–C7 = 1.396(3), C7–C8 = 1.417(3), C8–C9 = 1.403(3), C9–C4 = 1.415(3) Å). Based on the quality of the room temperature crystal structure of **1**, this difference in arene bond lengths may be significant and in support of the theory of alternating single and double character in the arene ring. However, analysis of the differences between the three shorter and three longer bonds indicated that only five of the nine differences are statistically different, based on a value of $3\Delta\sigma = 0.012$ Å. The difference between the averaged short and averaged long bonds is 0.014 Å, and this difference is statistically significant. It must be concluded that, although indicative, these alternating long and short bonds observed are not conclusive evidence for a localized bonding model for the arene in **1**. No endocyclic angular distortions are observed within the arene frame for **1** (largest deviation from 120° is observed for C5–C4–C9 = 120.7(2)°), contrary to that observed in [*cis*-$(CO)_4(PPh_3)Mn\{\mu\text{-}(\eta^1{:}\eta^6\text{-}C_6H_5)\}Cr(CO)_3$] where the manganese is σ-bonded to the benzene ring (largest deviation from 120° is 114.5(5)°) [9].

An interesting feature of the structure of **1** is the positioning of the $P(OMe)_3$ group on the same side of the molecule as the chromium tripodal moiety. By contrast, the PPh_3 ligand in the structure of [*cis*-$(CO)_4(PPh_3)Mn\{\mu\text{-}(\eta^1{:}\eta^6\text{-}C_6H_5)\}Cr(CO)_3$] and the $Cr(CO)_3$ moiety are on opposite sides of the arene ring [9], thereby placing the bulky phosphine on the more favoured open side of the benzene ring. Inspection of the phosphine ligand indicates that the geometry around the P–OC bonds is not symmetrical. The Mn–P–O10 angle of 119.6(1)° is significantly larger than the other two Mn–P–O angles: Mn–P–O11 = 112.3(3)° and Mn–P–O9 = 112.1(3)°. Furthermore, the angle O10–P–O11 (98.7(1)°) is significantly smaller than the other O–P–O angles: O9–P–O11 = 106.6(1)° and O9–P–O10 = 106.1(1)°. From Fig. 1 the arrangement of the three methoxy groups in the molecule and the different deformation of the P–O–C linkage (P–O10–C16) closest to the carbonyl (C1–O1) moiety are clearly visible. The torsion angle Mn–P–O10–C16 (73.0(2)°) is less than half the other corresponding angles Mn–P–O9–C15 (179.7(2)°) and Mn–P–O11–C17 (151.3(2)°), indicating a more *cis*-like orientation of this group relative to the more extended conformation of the other two methoxy groups. The intramolecular nearest-neighbour C–C(POMe)...O(CO) distance (C16–O1 is 3.490 Å) is significantly greater than the sum of the van der Waals radii for C–O, indicating no formal non-bonded interactions. A probable cause of this extreme dissimilarity could thus be the ability to minimise steric strain (interaction) between C16 and O1/O2 by assuming a position with the methoxy group directed between the oxygen atoms of the nearest carbonyls. Hunter and McLernon [18] and Heppert *et al.* [19] described similar types of interlocking 'molecular gear' arrangements for $(\eta^6\text{-}1,3,5\text{-}C_6H_3Fp_3)Cr(CO)_3$ and $(\eta^6\text{-}1,4\text{-}C_6H_4ClFp)Cr(CO)_3$ ($Fp = Fe(C_5H_5)(CO)_2$), respectively. This *endo*-placement of the $P(OMe)_3$ ligand may also be a result of the packing forces that occur during the crystallization process. Based on inspection of a model of this molecule, there is no obvious steric or electronic hindrance that could influence the rotation around the C9–C10 or C10–Mn bonds, and thus favouring a specific rotamer.

The arene–chromium fragment of **1** shows remarkable resemblance in structural features to the analogous complex [$(CO)_5Mn\{\mu\text{-}(\eta^1{:}\eta^6\text{-}C(O)C_6H_5)\}Cr(CO)_3$] [9], but differs in the orientation of the $Cr(CO)_3$ group with respect to the arene ring which is nearly perfectly staggered, as reflected by the following torsion angles: C1–Cr–CNTR–C9 = 26.2°, C2–Cr–CNTR–C7 = 24.7° and C3–Cr–CNTR–C5 = 24.3°. A near *anti* eclipsed conformation was recorded for the above-mentioned Cr–Mn complex [9], and is the anticipated and favoured conformation for non-directing ring substituents [20, 21]. The adoption of the generally energetically less favoured staggered conformation for $Cr(CO)_3$ in **1** could be ascribed to the close proximity of the methoxy group to carbonyl ligands.

The Mn–C(acyl) distance of 2.081(2) Å shows some carbene character but is significantly longer than the Mn–C(carbene) distance of 1.96(1) Å recorded for *cis*-[$Mn(CO)_4\{COCH_2CH_2O\}Cl$], and is identical to the

2.062(7)° reported for the σ-coordinated acyl ligand in $[Mn\{P(OPh)_3\}_3(CO)_2\{C(O)H\}]$ [22, 23]. Thus, the preference of the acyl carbonyl to align with the equatorial plane of the manganese ligand rather than maintaining coplanarity with the arene ring, is evidenced by all these observations. The Mn–C(carbonyl) bond distances of the carbonyls *trans* to the trimethylphosphite group (Mn–C12 = 1.820(3) Å) and the acyl unit (Mn–C14 = 1.834(2) Å) are shorter than the average distance (1.858(3) Å) for the other two Mn–C(carbonyl) bond lengths in the complex.

Supplementary material

Additional material available from author P.H.v.R. comprises anisotropic thermal parameters, bond lengths and angles for the non-hydrogen atoms, and hydrogen atom coordinates, together with their estimated standard deviations.

Acknowledgement

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