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Preparation and characterisation of cobalt (l) acyl compounds

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Abstract

The new cobalt (l) acyl compounds, $[Co(PMe_3)(CO)_3(COMe)]$ **1**, $[Co(PPhMe_2)(CO)_3(COMe)]$ **2**, $[Co(P(4\text{-}Me\text{-}C_6H_4)_3)(CO)_3(COMe)]$ **3** and $[Co(P(4\text{-}F\text{-}C_6H_4)_3)(CO)_3(COMe)]$ **4**, have been prepared from $[Na(Co(CO)_4)]$. The compound $[Co(PCy_3)(CO)_3(COMe)]$ **5** has been prepared from $[Co(PCy_3)(CO)_3(Me)]$ **6**. The crystal structures of **5** and **6** are reported.
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1. Introduction

Cobalt (l) alkyl [1] and acyl [2] compounds of the form $[Co(L)(CO)_3(R)]$ and $[Co(L)(CO)(COR)]$ have been extensively studied [3] with regard to the carbonylation and decarbonylation process. Their relevance to commercial applications, most notably in the hydroformylation [4,5] of olefins, has ensured continued interest. More recently, such acyl compounds have attracted renewed interest following the discovery that $[Co(PPh_3)(CO)_3(COMe)]$ [6] and $[Co(P(o\text{-}tolyl)_3)\text{-}(COMe)]$ [7] are pre-catalysts for aziridine/CO copolymerisation. However, despite the wealth of cobalt (l) acyl compounds in the literature [3], there are comparatively few examples [2,7,8] of tertiary phosphine substituted tricarbonyl cobalt (l) acyls containing the simple [COMe] moiety. Our interest in carbon–carbon bond formation led us to prepare and characterise a number of tertiary phosphine substituted cobalt (l) acyl complexes, as described below.

2. Results and discussion

*2.1. Synthesis of $[Co(L)(CO)_3(COMe)]$ $(L = PMe_3$ (**1**), $PPhMe_2$ (**2**), $P(4\text{-}Me\text{-}C_6H_4)_3$ (**3**), $P(4\text{-}F\text{-}C_6H_4)_3$ (**4**), PCy_3 (**5**)) and $[Co(PCy_3)(CO)_3(Me)]$ (**6**)*

The new cobalt (I) acyl complexes $[Co(PMe_3)(CO)_3(COMe)]$ **1**, $[Co(PPhMe_2)(CO)_3(COMe)]$ **2**, $[Co(P(4\text{-}Me\text{-}C_6H_4)_3)(CO)_3(COMe)]$ **3** and $[Co(P(4\text{-}F\text{-}C_6H_4)_3)\text{-}(CO)_3(COMe)]$ **4** were prepared by treating $[Na(Co(CO)_4)]$ with an excess of MeI and 1 equivalent the appropriate tertiary phosphine in diethyl ether at either 0 °C (**3–4**) or −78 °C (**1–2**) (Scheme 1).

These syntheses are analogous to those used to prepare $[Co(PPh_3)(CO)_3(COMe)]$ [2]. Reduction of $[Co(PCy_3)(CO)_3]_2$ over Na/Hg amalgam followed by treatment with MeI (Scheme 2) gave $[Co(PCy_3)\text{-}(CO)_3(Me)]$ **6**.

The compound $[Co(PCy_3)(CO)_3(COMe)]$ **5** was synthesised by passing CO through an ethereal solution of **6**. Characterisation was achieved by IR and NMR spectroscopies, by mass spectrometry and by microanalysis. These characterising data are summarised in Table 1. The X-ray crystal structures of compounds **5** and **6** have been determined.

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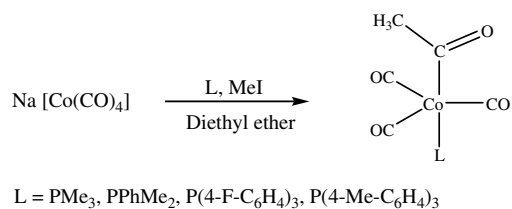
Scheme 1. Synthetic route for direct synthesis of cobalt (I) acyl compounds 1–4.

L = PMe$_3$, PPhMe$_2$, P(4-F-C$_6$H$_4$)$_3$, P(4-Me-C$_6$H$_4$)$_3$

2.2. Spectroscopic data

The IR spectra in Nujol of compounds 1–5 can be assigned by analogy with those of previously reported cobalt (l) acyl complexes [3]. The compounds 1–5 all exhibit three bands (see Table 1) in the region 1950–2050 cm^{-1}, assignable to $v(CO)_{terminal}$. This is consistent with C_{3V} symmetry with the three terminal carbonyl groups in the equatorial positions, and with a *trans*
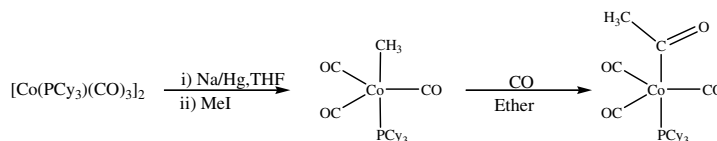
Scheme 2. Synthetic route for compounds 5 and 6.

Table 1
Summary of analytical data for the compounds 1–6

Compound[a]	NMR data[b]
1 [Co(PMe$_3$)(CO)$_3$(COMe)] Orange oil C, 36.3 (36.7); H, 4.4 (4.6); N, 0 (0) Mass (EI): 262 [M]$^+$ IR: 1686m, 1954 s, 1976 s, 2046 w	^{1}H: 1.45 [d, $^2J_{PH}$ = 9.71, 9H, P(C*H*$_3$)$_3$], 2.64 [s, 3H, C(O)C*H*$_3$] ^{31}P{^{1}H}:10.87 [s, P(C*H*$_3$)$_3$] ^{13}C{^{1}H}: 19.17 [d, J_{PC} = 27.62 Hz, P(C*H*$_3$)$_3$], 50.90 [d, $^3J_{PC}$ = 26.93, C(O)C*H*$_3$], 200.03 [br s, CoC*O*], 240.67 [d, $^2J_{PC}$ = 32.4, *C*(O)CH$_3$]
2 [Co(PPhMe$_2$)(CO)$_3$(COMe)] Yellow solid C, 48.3(48.2); H,4.5(4.4); N 0(0) Mass (FI): 296 [M − CO]$^+$; 268 [M − (CO)$_2$]$^+$ IR 1686 m, 1956 s, 1976 s, 2036 w	^{1}H: 1.73 [d, $^2J_{PH}$ = 9.24, 6H PPh(C*H*$_3$)$_2$], 2.67 [s, 3H, C(O)C*H*$_3$], 7.50 [m, 3H Ar*H*], 7.64 [m, 2H Ar*H*] ^{31}P{^{1}H}:20.10 [s, *P*Ph(CH$_3$)$_2$] ^{13}C{^{1}H}:16.93 [d,$^1J_{PC}$ = 28.53, PPh(C*H*$_3$)$_2$], 49.39 [d, $^3J_{PC}$ = 25.14, C(O)C*H*$_3$], 129.08 [m, Ar*C*], 136.24 [d, $^1J_{PC}$ = 42.31, Ar*C*] 200.38 [br s, CoC*O*], 240.68 [d, $^2J_{PC}$ = 33.43, *C*(O)CH$_3$]
3 [Co(P(4-F-C$_6$H$_4$)$_3$)(CO)$_3$(COMe)] Yellow solid C, 55.2 (55.0), H, 3.2 (3.0), N 0 (0) Mass (FI); 474 [M − CO]$^+$, 445 [M − (CO)$_2$]$^+$ IR: 1674 m, 1954 s, 1990 s, 2052 w	^{1}H: 2.69 [s, 3H, C(O)C*H*$_3$], 7.13 (dt, $^2J_{HH}$ = 8.51, $^3J_{FH}$ = 1.76, 2H, *m*-Ar*H*), 7.33 (m, 2H, *o*-Ar*H*) ^{19}F{^{1}H}:-108.36 [s, P(4-*F*-C$_6$H$_4$)$_3$] ^{31}P{^{1}H}:48.80 [s, *P*(4-F-C$_6$H$_4$)$_3$] ^{13}C{^{1}H}:49.43 [d, $^3J_{PC}$ = 28.72, 3H, C(O)C*H*$_3$], 116.2 [m, Ar*C*], 128.89 [d, J = 3.41, Ar*C*], 129.46 [d, J = 3.41, Ar*C*], 135.0[m, Ar*C*], 162.65 [d, J = 1.97, Ar*C*], 166.00 [d, J = 2.12, Ar*C*], 199.68 [d, $^2J_{PC}$ = 18.98 Co(C*O*)$_3$], 231.74 [d, $^2J_{PC}$ = 31.16, *C*(O)CH$_3$]
4 Co(CO)$_3$(P(4-Me-C$_6$H$_4$)$_3$)(COMe) Yellow solid C, 63.7 (63.3) H, 5.0 (5.0) N 0 (0) Mass (FI): 462 [M − CO]$^+$, 434 [M − (CO)$_2$]$^+$ IR: 1670 m, 1948 s, 1972 s, 2042 w	^{1}H :2.37 [s, 9H, 4-C*H*$_3$-C$_6$H$_5$]; 2.74 [s, 3H, C(O)C*H*$_3$] ; 7.311[m, 12H, Ar*H*] ^{31}P{^{1}H}:48.63 [s, *P*(CH$_3$)$_3$] ^{13}C{^{1}H}:21.45 [s, 4-*C*H$_3$-C$_6$H$_5$], 50.32 [d, $^3J_{PC}$ = 26.28, C(O)C*H*$_3$], 129.75 [d, J_{PC} = 10.13, Ar*C*], 130.49 [d, J_{PC} = 44.63, Ar*C*], 130.40 [s, Ar*C*], 130.99 [s, Ar*C*], 141.59 [s, Ar*C*], 199.80 [br s, CoC*O*], 238.70[d, $^2J_{PC}$ = 32.61, *C*(O)CH$_3$]
5 [Co(PCy$_3$)(CO)$_3$(COMe)] Yellow solid C, 59.6 (59.2) H, 8.6 (7.8) N 0 (0) Mass (FI): 438 [M − CO]$^+$, 410 [M − (CO)$_2$]$^+$ IR: 1682 m, 1946 s, 1969 s, 2038 w	^{1}H ; 2.75 [d, $^4J_{PH}$ = 0.58, 3H, C(O)C*H*$_3$], 1.04-1.89 [m, 33H, P(C$_6$*H*$_{11}$)$_3$] ^{31}P{^{1}H}:60.91 [s, *P*(C$_6$H$_{11}$)$_3$] ^{13}C{^{1}H}:26.31 [s,P(C$_6$*H*$_{11}$)], 27.62 [d, J_{PC} = 10.1, P(C$_6$*H*$_{11}$)], 36.70 [d, J_{PC} = 16.6, P(C$_6$*H*$_{11}$)], 48.68 [d, J_{PC} = 23.6, C(O)C*H*$_3$], 201.54 [d, J_{PC} = 15.90, CoC*O*], 235.55 [d, J_{PC} = 29.06, *C*(O)CH$_3$]
6 [Co(PCy$_3$)(CO)$_3$(Me)] Yellow solid C, 60.7 (60.3) H, 8.3 (8.3) N 0 (0) Mass (FI): 438 [M]$^+$ IR: 1948 s, 2022 w	^{1}H ; 0.26 [s,3H, C*H*$_3$], 1.04-1.89 [m, 33H, P(C$_6$*H*$_{11}$)$_3$] ^{31}P{^{1}H}:74.23 [s, *P*(C$_6$H$_{11}$)$_3$] ^{13}C{^{1}H}:-9.23 [d, J_{PC} = 16.77, CoC*H*$_3$], 26.31 [s,P(C$_6$*H*$_{11}$)], 27.62 [d, J_{PC} = 10.1, P(C$_6$*H*$_{11}$)], 36.70 [d, J_{PC} = 16.62, P(C$_6$*H*$_{11}$)], 48.68 [d, J_{PC} = 23.6, C(O)C*H*$_3$], 201.54 [d, J_{PC} = 15.94, CoC*O*], 235.55 [d, J_{PC} = 29.06, *C*(O)CH$_3$]

[a] Analytical data given as found (calculated) in %, IR data (cm^{-1}) determined for Nujol mulls on KBr discs.
[b] The NMR data (CD$_2$Cl$_2$, 298 K), 1–4, (C$_6$D$_6$, 298 K), 5 and 6, given as [multiplicity in Hz, relative intensity, assignment].

position of the acyl and phosphine groups [9], along the axis. Typically, the two strong bands are assigned to the E mode and the weak band is assigned to the A_1 totally symmetric stretch [10]. In all instances, the E band is split into two separate bands and this has been attributed to hindered rotation of the acyl group about the Co–C bond, due to $d\pi$-$p\pi$ bonding between the acyl group and the cobalt centre [11]. A further band assigned to $v(CO)_{acyl}$ is observed between 1670 and 1686 cm^{-1}, the lower stretching frequency reflecting the lower bond order of the CO_{acyl} compared with the $CO_{terminal}$.

The ^{1}H NMR spectra for compounds 1–5 show characteristic resonances between δ 2.64 and δ 2.76, which are assigned to the acyl methyl group. The ^{13}C{H} for 1–5 show characteristic $CO_{terminal}$ (ca. δ 200), CO_{acyl} (ca. δ 240) and CH$_3$ (ca. δ 50) resonances. In all instances, the coupling of the ^{31}P{H} nucleus to the methyl carbon of the *trans* acyl was observed. $^3J_{PC}$ values were in the range 23–28 Hz. Coupling of the ^{31}P{H} nucleus to the carbon nucleus of CO_{acyl} was also observed in all instances ($^2J_{PC}$ = 29–33 Hz). Curiously, the ^{13}C{H} resonances attributed to the $CO_{terminal}$ for the compounds 1–4 showed broad singlets. This may be due to quadropolar broadening. By contrast, for compound 5 the ^{13}C{H} resonance attributed to $CO_{terminal}$ is observed as a doublet, indicating coupling with the ^{31}P{H} nucleus. In this series of compounds, the $CO_{terminal}$ ^{13}C{H} resonances are less susceptible than the CO_{acyl} ^{13}C{H} resonances to steric and electronic influences of the appended ligand. The former varying by a maximum of 1.5 ppm for the compounds 1–5, whereas the later showed variation of ca. 10 ppm. This reflects the *trans* influence of the mutually axial ligand and acyl group.

In all instances FI or ES$^+$ spectra of compounds 1–5 showed either the [M]$^+$ or [M − CO]$^+$ and [M − 2CO]$^+$ ions.

Table 2
Summary of crystallographic data for the compounds 5 and 6

	5	6
Empirical formula	C$_{23}$H$_{36}$CoO$_4$P	C$_{22}$H$_{36}$CoO$_3$P
Formula weight	466.44	438.43
Temperature (K)	150	150
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P\,2_1/n$	$P\,2_1/n$
Unit cell dimensions		
a (Å)	14.9641(2)	20.0898(3)
b (Å)	10.4925(2)	11.5044(2)
c (Å)	16.4305(3)	20.6298(3)
α (°)	90	90
β (°)	113.5830(8)	111.0245(6)
γ (°)	90	90
Cell volume (Å^3)	2364.31(7)	4450.56(12)
Z	4	8
Calculated density (mg/m^3)	1.310	1.309
Absorption coefficient (mm^{-1})	0.818	0.862
F_{000}	992	1872
Crystal size (mm)	$0.16 \times 0.24 \times 0.24$	$0.12 \times 0.14 \times 0.14$
Description of crystal	Pale-yellow fragment	Pale-brown block
Absorption correction	Semi-empirical from equivalent reflections	Semi-empirical from equivalent reflections
Transmission coefficients (min, max)	0.82, 0.88	0.89, 0.90
θ Range for data collection (°)	$5.0 \leqslant \theta \leqslant 27.5$	$5.0 \leqslant \theta \leqslant 27.5$
Index ranges	$-19 \leqslant h \leqslant 17, 0 \leqslant k \leqslant 13, 0 \leqslant l \leqslant 21$	$-26 \leqslant h \leqslant 24, -14 \leqslant k \leqslant 14, 0 \leqslant l \leqslant 26$
Reflections measured	24020	20105
Unique reflections	5649	10617
R_{int}	0.036	0.082
Observed reflections ($I > 3\sigma\,(I)$)	3918	6644
Refinement method	Full-matrix least-squares on F	Full-matrix least-squares on F
Parameters refined	262	512
Weighting scheme	Chebychev 3-term polynomial	Chebychev 3-term polynomial
Goodness-of-fit	1.0837	1.0324
R	0.0266	0.0490
wR	0.0293	0.0525
Residual electron density (min, max) (e Å^{-3})	−0.27, 0.35	−0.55, 0.59

2.3. X-ray crystallography of 5 and 6

Crystals suitable for X-ray structure determination were grown by cooling saturated pentane solutions of **5** and **6** to −80 °C. Selected structural parameters for compounds **5** and **6** are given in Table 2. A view of the X-ray crystal structure of **5** is given in Fig. 1. Selected bond lengths and angles for compound **5** are given in Table 3. Table 4 lists selected bond lengths and angles of similar cobalt (l) acyl complexes. The compound **5** shows a distorted trigonal bipyramidal structure with three carbonyl groups in equatorial positions, and the PCy_3 and acyl groups occupying mutually axial positions.
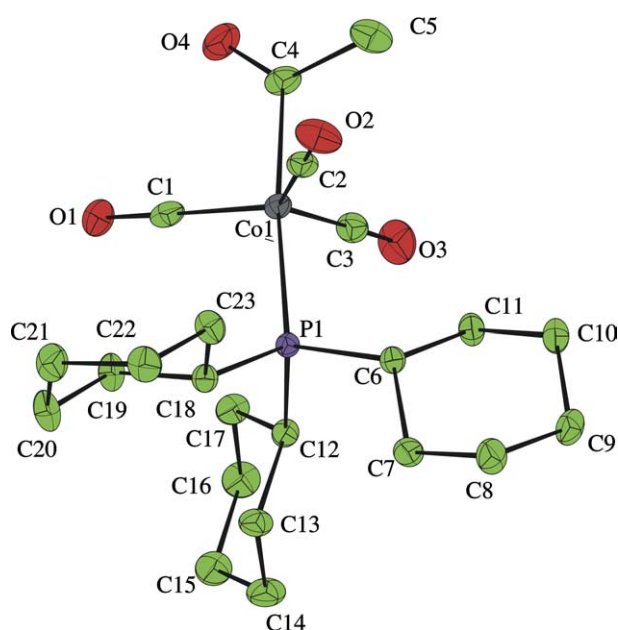

Fig. 1. ORTEP diagram of the molecular structure of compound **5**. Thermal ellipsoids are drawn at 40%. Hydrogen atoms have been omitted for clarity.

Table 3
Selected bond lengths (Å) and angles (°) for 5

Compound 5	
Co(1)–C(1)	1.8014(18)
Co(1)–C(2)	1.7726(17)
Co(1)–C(3)	1.7755(18)
Co(1)–C(4)	2.0149(17)
Co(1)–P(1)	2.2753(4)
C(1)–O(1)	1.141(2)
C(2)–O(2)	1.147(2)
C(3)–O(3)	1.150(2)
C(4)–O(4)	1.194(2)
C(4)–Co(1)–P(1)	172.95(6)
C(1)–Co(1)–C(4)	90.67(8)
C(2)–Co(1)–C(4)	84.52(7)
C(3)–Co(1)–C(4)	86.59(7)

Table 4
Selected bond lengths (Å) of cobalt (l) acyl compounds

Compound	Bond lengths (Å)		
	Co–C$_{acyl}$	Co–P	C=O$_{(acyl)}$
$[Co(PCy_3)(CO)_3(COMe)]$	2.0149(17)	2.2753(4)	1.194(2)
$[Co(PPh_3)(CO)_3(COMe)]$ [7]	1.988(6)	2.249(4)	1.195(7)
$[Co(PPh_3)(CO)_3(C(O)CH_2Cl)]$ [13]	1.999 (5)	2.25(4)	1.180[a]
$[Co(PPh_3)(CO)_3(C(O)O^nBu)]$ [10]	1.967(2)	2.229(1)	120.1(2)
$[Co(PPh_3)(CO)_3(C(O)OMe)]$ [14]	1.976[a]	2.234[a]	1.196[a]

[a] Esd not given.

The equatorial CO groups are slightly bent towards the axial acyl group, with an average $C_{carbonyl}$–Co–C_{acyl} bond angle of 87.4°. This can be attributed to the more sterically demanding nature of the phosphine ligand compared with the smaller *trans* acyl group. A similar, though more pronounced effect has been noted in $[Co(PPh_3)(CO)_3H]$ and $[Co(PCy_3)(CO)_3H]$ [12] with average C–Co–H bond angles of 81.6° and 81°, respectively. In the related compound $[Co(PPh_3)(CO)_3(COMe)]$ [7], the average $C_{carbonyl}$–Co–C_{acyl} angle is 87.9°.

The crystal structure of **6** is somewhat unusual in that two crystallographically distinct molecules are observed in the unit cell. Views of these molecules are given in Figs. 2a and b. Selected bond lengths and angles for **6** are given in Table 5. The distinct molecules differ by the orientation of one of the cyclohexyl groups (C(11)–C(16)/C(33)–C(39)), but the two molecules are otherwise related by a non-crystallographic[1] 180° rotation. A similar occurrence has been reported by Zucchi et al. [15] in $[Co(PPh_3)(CO)_3(CH_2C_6H_4{}^tBu)]$, who noted that this effect may be correlated to the unexpected stereochemistry observed for $[Co(PPh_3)(CO)_3(CH_2(O)COR)]$ complexes. However, since $[Co(PPh_3)(CO)_3(CH_2C_6H_4{}^tBu)]$ and $[Co(PCy_3)(CO)_3(Me)]$ both contain symmetrical organic ligands a direct comparison is not possible. Compound **6** shows the expected distorted trigonal bipyramidal geometry, with three terminal carbonyl groups in the equatorial positions, and the alkyl and phosphine ligands in axial sites. The terminal carbonyl groups are bent towards the less sterically demanding methyl group, with an average $C_{carbonyl}$–Co–C_{alkyl} angle of 84.25°. This indicates an approximately 6° bend towards the alkyl group presumably due to the more sterically demanding PCy_3 ligand. In general, the Co–C_{alkyl} and Co–P bonds show the most sensitivity to changes in the tertiary phosphine and organic ligand [15]. The lack of crystallinity/stability of methyl substituted cobalt compounds makes direct comparisons difficult. However, Table 6 lists selected bond lengths and angles for related cobalt (l) alkyl compounds. In the compound **6**, the 2.081(3) Å Co–C_{alkyl}

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[1] i.e., not a symmetry element of the unit cell.
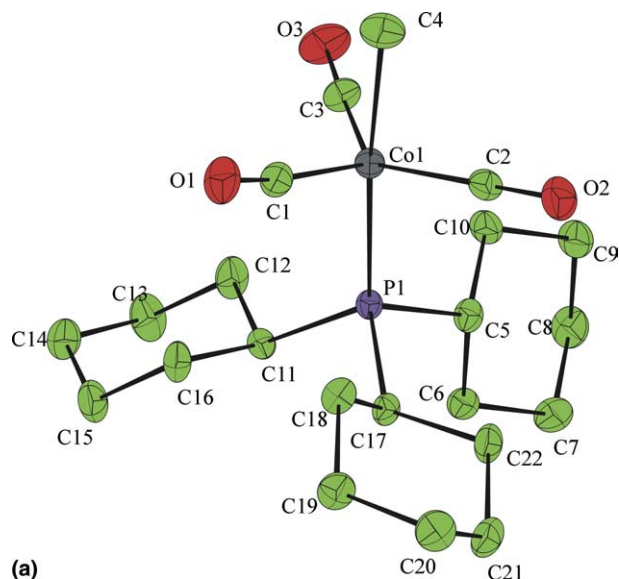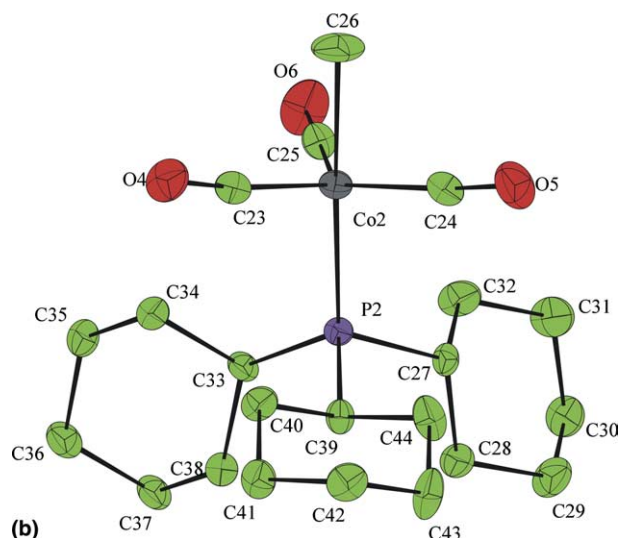
Fig. 2. (a) ORTEP diagram of distinct molecule a of compound **6**. Thermal ellipsoids are drawn at 40%. Hydrogen atoms have been omitted for clarity. (b) ORTEP diagram of distinct molecule b of compound **6**. Thermal ellipsoids are drawn at 40%. Hydrogen atoms have been omitted for clarity.

bond is longer than is observed in most of the characterised PPh$_3$ containing cobalt (l) alkyls, though shorter than that observed for [Co(PPh$_3$)(CO)$_3$(CH$_2$C$_6$H$_4$$'$Bu)].

Table 5
Selected bond lengths (Å) and angles (°) for compound **6**

Molecule a		Molecule b	
Co(1)–C(4)	2.081(3)	Co(2)–C(26)	2.081(3)
Co(1)–P(1)	2.2291(8)	Co(2)–P(2)	2.2311(8)
C(1)–O(1)	1.131(4)	C(23)–O(4)	1.136(4)
C(2)–O(2)	1.149(4)	C(24)–O(5)	1.139(4)
C(3)–O(3)	1.146(4)	C(25)–O(6)	1.141(4)
Co(1)–C(1)	1.792(3)	Co(2)–C(23)	1.788(3)
Co(1)–C(2)	1.772(3)	Co(2)–C(24)	1.783(4)
Co(1)–C(3)	1.781(3)	Co(2)–C(25)	1.779(4)
C(4)–Co(1)–P(1)	175.03(12)	C(26)–Co(2)–P(2)	177.89(14)
C(1)–Co(1)–C(4)	84.06(15)	C(23)–Co(2)–C(26)	84.02(17)
C(2)–Co(1)–C(4)	85.90(15)	C(24)–Co(2)–C(26)	84.43(17)
C(3)–Co(1)–C(4)	82.81(16)	C(25)–Co(2)–C(26)	84.10(17)

The 2.2291(8)/2.2311(8) Co–P bond length is in the typical range observed for this type of compound.

3. Conclusion

New cobalt (l) acyl compounds, [Co(L)(CO)$_3$-(COMe)] (L = PMe$_3$ **1**, PPhMe$_2$ **2**, P(4-F-C$_6$H$_4$)$_3$ **3**, P(4-Me-C$_6$H$_4$)$_3$ **4**, PCy$_3$ **5**) and the alkyl complex [Co(PCy$_3$)(CO)$_3$(Me)] **6** have been synthesised and characterised.

4. Experimental

4.1. General procedures

All manipulations were carried out under N$_2$, using conventional Schlenk-line techniques. PMe$_3$ [18], P(4-Me-C$_6$H$_4$)$_3$ [19] and [Na(Co(CO)$_4$)] [20] were prepared according to the literature methods. The compound Co$_2$(CO)$_8$ was purchased from Strem and used as received. PPh$_3$, PPhMe$_2$, P(4-F-C$_6$H$_4$)$_3$, PCy$_3$ and MeI were purchased from Aldrich Chemical Co. and used as received. [Co(PCy$_3$)(CO)$_3$]$_2$ was synthesised by refluxing Co$_2$(CO)$_8$ and PCy$_3$ in toluene. NMR spectra were recorded on either a 300 MHz Varian Mercury or a 500 MHz Varian Unity spectrometer, referenced internally using the residual protio-solvent, (^{1}H and ^{13}C, $\delta = 0$), or externally BF$_3 \cdot$ Et$_2$O (^{11}B, $\delta = 0$), H$_3$PO$_4$

Table 6
Selected bond lengths (Å) of cobalt (l) alkyl compounds

Compound	Bond lengths (Å)		
	Co–C$_{alkyl}$	Co–P	C=O$_{(terminal)\ ave}$
[Co(PCy$_3$)(CO)$_3$(Me)]	2.081(3), 2.081(3)	2.2291(8), 2.2311(8)	1.142(4), 1.139(4)
[Co(PPh$_3$)(CO)$_3$(CH$_2$Cl)] [13]	2.022(3)	2.223(1)	1.138(3)
[Co(PPh$_3$)(CO)$_3$(CH$_2$C$_6$H$_4$^{t}Bu)] [15]	2.120(4), 2.136(5)	2.2213(13), 2.313(13)	1.141(6), 1.137(6)
[Co(PPh$_3$)(CO)$_3$(C$_6$F$_5$)] [16]	2.011(2)	2.2218(6)	1.140(3)
[Co(PPh$_3$)(CO)$_3$(CF$_3$)] [17]	1.953(6)	2.235(1)	1.174(7)

(^{31}P, $\delta = 0$) and CFCl$_3$ (^{19}F, $\delta = 0$) and chemical shifts were reported with respect to SiMe$_4$. All chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Infrared spectra were recorded on a Perkin–Elmer 1600 FTIR. Elemental analyses and mass spectra were provided by the Microanalytical Services of the Inorganic Chemistry Laboratory, Oxford.

4.2. Preparation of [Co(PMe$_3$)(CO)$_3$(COMe)] (1)

The compound Na[Co(CO)$_4$] (500 mg, 2.54 mmol) in diethyl ether (40 ml) at −78 °C was treated with neat PMe$_3$ (0.32 ml, 2.54 mmol). The mixture was allowed to warm to room temperature under stirring for 20 min and was then again cooled to −78 °C and neat MeI (1.6 ml, 25.4 mmol) was added. The solution was allowed to warm to room temperature under stirring, a white precipitate formed. After 30 min of stirring, the mixture was filtered and solvents were removed under reduced pressure to leave an oily yellow solid. This was dissolved in diethyl ether (20 ml) and cooled to −78 °C. Pentane was added (10 ml) and yellow crystals separated. These were isolated by filtration and dried in vacuo. On warming to room temperature, the crystals melted to give 7 as an orange oil. Yield = 269 mg (40.5%).

4.3. Preparation of [Co(PPhMe$_2$)(CO)$_3$(COMe)] (2)

A solution of Na[Co(CO)$_4$] (500 mg, 2.54 mmol) in diethyl ether (40 ml) was cooled to −78 °C. Neat PPhMe$_2$ (0.46 ml, 2.54 mmol) was added and the mixture allowed to warm to room temperature under stirring for 20 min. The solution was then cooled to −78 °C and neat MeI (1.6 ml, 25.4 mmol) was added. The solution was again allowed to warm to room temperature under stirring. During this time a white precipitate formed and the solution turned brown. After 1 h stirring the mixture was filtered and solvents were removed under reduced pressure to leave sticky brown oil, which was recrystallised from pentane at −78 °C to give a yellow/brown solid. Yield = 411 mg (50.1%).

4.4. Preparation of [Co(P(4-F-C$_6$H$_4$)$_3$)- (CO)$_3$(COMe)] (3)

A solution of Na[Co(CO)$_4$] (500 mg, 2.54 mmol) in THF (40 ml) was cooled to 0 °C and P(4-F-C$_6$H$_4$)$_3$ (802 mg, 2.54 mmol) was then added in one portion. The mixture was stirred for 10 min during which time the solution darkened. MeI (1.6 ml, 25.4 mmol) was then added, leading to the formation of an orange solution. This was left stirring for 17 h and allowed to warm to room temperature, leading to the formation of a pale yellow mixture. This was filtered, leaving a pale yellow solid. Recrystallisation from THF/pentane at −78 °C

left a pale yellow powder, which was dried under vacuum. Yield = 548 mg (43.2%).

4.5. Preparation of [Co(P(4-Me-C$_6$H$_4$)$_3$)- (CO)$_3$(COMe)] (4)

A solution of Na[Co(CO)$_4$] (650 mg, 3.29 mmol) in diethyl ether (40 ml) was cooled to 0 °C. A solution of P(4-Me-C$_6$H$_4$)$_3$ (1000 mg, 3.29 mmol) in diethyl ether (20 ml) was then added and the resulting solution left stirring for 5 min. Neat MeI (1.6 ml, 25.4 mmol) was then added and the solution left stirring at 0 °C for 1 h during which a white precipitate formed. The resulting mixture was filtered and solvent was removed under reduced pressure. This resulting yellow solid was dissolved in diethyl ether (10 ml) and filtered. Removal of solvents under reduced pressure left a yellow solid that was recrystallised from diethyl ether/pentane at −78 °C and dried under vacuum. Yield = 516 mg (32.3%).

4.6. Preparation of [Co(PCy$_3$)(CO)$_3$(COMe)] (5)

Carbon monoxide was passed through a solution of [Co(PCy$_3$)(CO)$_3$(Me)] (100 mg, 0.228 mmol) in diethyl ether (30 ml). Solvent was removed in vacuo and the resulting yellow solid was recrystallised from pentane at −80 °C to give the desired product as yellow crystals. These were isolated by filtration and dried under vacuum to yield 95.2 mg of 6. Crystals suitable for single crystal X-ray diffraction were grown by cooling a saturated pentane solution to −80 °C. Yield = 95.2 mg (89.5%).

4.7. Preparation of [Co(PCy$_3$)(CO)$_3$(Me)] (6)

A solution of [Co(PCy$_3$)(CO)$_3$]$_2$ (600 mg, 0.88 mmol) in THF (20 ml) was stirred over excess of Na/Hg amalgam for 17 h. The resulting suspension was allowed to settle before being transferred by cannular. MeI (1.5 ml) was added to resulting brown solution, which was stirred for 3 h. Removal of solvents yielded a dirty brown solid. This was extracted into pentane and cooled to −80 °C. The resulting yellow crystalline solid was isolated by filtration and dried under vacuum to yield 300 mg of 5. Crystals suitable for single crystal X-ray diffraction were grown by cooling a saturated pentane solution to −80 °C. Yield = 300 mg (38.9%).

5. X-ray crystallography

In each case, a single crystal was selected under inert atmosphere, encased in perfluoro-polyether oil, and mounted on the end of a glass fibre. Data were collected at 150 K using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated MoKα radiation,

$\lambda = 0.71073$ Å), as summarised in Table 2. The images were processed with the DENZO and SCALEPACK programs [21]. Corrections for all solution, refinement, and graphical calculations were performed using the CRYSTALS [22] program suite. The structures were solved by direct methods using the SIR 92 [23] program and refined by full-matrix least squares procedure on F. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters. Data for compound **6** indicated twinning of the crystal. The contributions of the two twin components to those reflections for which both diffraction patterns overlapped were included in the refinement, giving volume fractions of 0.754(12) and 0.246(12). The methyl hydrogen atoms were located in a difference Fourier map and their coordinates and isotropic thermal parameters subsequently refined.

6. Supplementary data

Crystallographic data for **5** and **6** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 261445 and 261446. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax:+44 1223 336033.

Acknowledgements

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