SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF ACETATOBIS(TRIPHENYLPHOSPHINE)DICARBONYLRHENIUM(I). NEW CARBOXYLATO DERIVATIVES OF RHENIUM(I) *

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Summary

Acetatobis(triphenylphosphine)dicarbonylrhenium(I), $(PPh_3)_2(CO)_2Re(O_2CCH_3)$, has been prepared in a novel way by treating $(PPh_3)_2(CO)_2Re(NHCOR)$ ($R = C_6H_5$, $p\text{-}MeC_6H_4$) with triethylamine and water in the presence of air. Oxidation of the ethyl group of the tertiary amine is presumably involved in the formation of the acetate ligand. Three-dimensional single-crystal X-ray diffraction analysis shows that the complex is octahedral with the phosphines in *trans* positions and the acetate ion acting as a chelating ligand. The complex crystallizes in the $P2_1/c$ space group with cell dimensions $a = 17.63(2)$, $b = 9.72(1)$, $c = 20.95(2)$ Å, $\beta = 104°38'(6')$, $Z = 4$. The mean values of bond lengths observed are Re—P 2.415, Re—O 2.21 and Re—(CO) 1.85 Å. The same acetate derivative and a series of carboxylato complexes $(PPh_3)_2(CO)_2Re(O_2CR')$ have been obtained from reactions of $Re(CO)_2(PPh_3)_3H$ with carboxylic acids R'COOH ($R' = H$, CH_3, CH_2Cl, CH_2CH_3, C_6H_5). When trifluoroacetic acid is used, a product of formula $(PPh_3)_2(CO)_3Re(OC(O)CF_3)$ is isolated.

The action of neutral ligands L on some of these products gave rise to derivatives of formula $(PPh_3)_2(CO)_2(L)Re(OC(O)R')$ ($L = CO$, $R' = H$, CH_3, C_6H_5; $L = p\text{-}MeC_6H_4NC$, $R' = CH_3$), having monodentate carboxylato moieties.

Introduction

In the course of our studies on the reactions of organic azides with transition metal complexes in low oxidation states [1], we recently succeeded in isolating rhenium(I) amido complexes of formula $(PPh_3)_2(CO)_2Re(NHCOR)$ (R = C_6H_5, p-MeC_6H_4) by reacting $Re(CO)_2(PPh_3)_3H$ with aroyl azides $RCON_3$ [2]. During our investigations on the reactivity of these complexes towards amines [2], an abnormal reaction path was observed when a tertiary amine, such as NEt_3, was used. We report here on the full characterization of the product of this reaction, which unexpectedly has been shown to be the acetatobis(triphenylphosphine)-dicarbonylrhenium(I), $(PPh_3)_2(CO)_2Re(O_2CCH_3)$, containing a chelating acetate ligand.

The same product and related carboxylato derivatives $(PPh_3)_2(CO)_2Re(O_2CR')$ are obtained from the reaction of $Re(CO)_2(PPh_3)_3H$ with organic acids $R'COOH$ (R' = H, CH_2Cl, CH_2CH_3, C_6H_5).

Experimental

Synthesis and reactions of carboxylate complexes of rhenium(I)

$Re(CO)_2(PPh_3)_3H$ was prepared as described in the literature. The IR and NMR spectra were obtained using Beckman model 33 and Perkin—Elmer model 237 spectrophotometers and a Varian NV-14 instrument operating at 60 MHz, respectively. Analytical data are reported in Table 1.

TABLE 1. ANALYTICAL DATA

Compound	Colour	M.p. (°C)	Elemental analyses Found (calcd.) (%)		Mol. wt. Found (calcd.) (%)
			C	H	
$(PPh_3)_2(CO)_2Re(O_2CH)$ (I)	Pale yellow	193	57.9 (57.7)	3.67 (3.83)	842 [a] (811)
$(PPh_3)_2(CO)_2Re(O_2CCH_3)$ (II) [b,c]	White	230	58.17 (58.2)	4.07 (4.00)	810 [d] (825)
$(PPh_3)_2(CO)_2Re(O_2CCH_2Cl)$ (III)	Pale pink	216	55.15 (55.2)	3.40 (3.73)	920 [a] (859.5)

(PPh₃)₂(CO)₂Re(O₂CH) (I)

Formic acid (5 ml) was added to a suspension of $Re(CO)_2(PPh_3)_3H$ (0.1 g) in ethanol (50 ml). The suspension was stirred overnight and the pale yellow insoluble compound was recovered by filtration, washed with ethanol and dried in vacuo.

(PPh₃)₂(CO)₂Re(O₂CCH₃) (II)

(a). To a benzene solution (60 ml) of $(PPh_3)_2(CO)_2Re(NHCOR)$ (0.2 g) (R = C_6H_5 or p-MeC_6H_4) [2] were added triethylamine (previously distilled over KOH) (15 ml) and water (5 drops) and the suspension stirred for 15 h in air. The resulting solution was evaporated to dryness and the residue washed with ethanol. II was recovered as an insoluble white product, while the mother liquor, when evaporated to dryness, gave a residue which was shown to be benzoyl or toluoyl amide by comparison of its IR spectrum with those of authentic samples. The reaction proceeded similarly when commercial NEt_3 was used.

(b). To a suspension of $Re(CO)_2(PPh_3)_3H$ (1.0 g) in ethanol (70 ml) were added acetic acid (3 ml) and water (10 drops). The suspension was maintained at 45—50°C for 4 h with stirring and then cooled. II was filtered off, washed with ethanol and dried in vacuo.

(PPh₃)₂(CO)₂Re(O₂CCH₂Cl) (III)

(a). The pale pink compound was obtained using the same method as that described for I.

(b). It could also be prepared by stirring an ethanol suspension of II to which monochloroacetic acid had been added for 5 h at 60°C.

(PPh₃)₂(CO)₂Re(O₂CCH₂CH₃) (IV)

Propionic acid (1 ml) was added to a suspension of $Re(CO)_2(PPh_3)_3H$ (0.4 g) in a benzene/ethanol 1 : 3 mixture (50 ml). This suspension was maintained at 50°C for 6 h with stirring. The resulting solution was evaporated to ca. 10 ml and IV obtained as an insoluble product, which was filtered off, washed with ethanol and dried in vacuo.

(PPh₃)₂(CO)₂Re(O₂CC₆H₅) (V)

The solution was stirred for 2 h and then evaporated to dryness. The oily residue was treated with n-hexane giving compound IX as an insoluble product, which was washed with n-hexane and dried in vacuo.

$(PPh_3)_2(CO)_3Re(OC(O)CF_3)$ (X)

A few drops of trifluoroacetic acid were added to a benzene/ethanol 1 : 3 mixture (70 ml) with $Re(CO)_2(PPh_3)_3H$ (0.15 g). The mixture was maintained at 45°C for 1 h and the resulting solution evaporated to ca. 20 ml giving compound X as an insoluble product, which was filtered off, washed with ethanol and dried in vacuo.

Reaction of VII with $NaBH_4$

To an ethanol suspension (40 ml) of compound VII (0.08 g) were added triphenylphosphine (0.05 g) and sodium borohydride (0.03 g), and the mixture stirred for 3 h. A white product was filtered off, washed with ethanol and dried in vacuo. Its IR spectrum was identical to that of an authentic sample of $Re(CO)_2(PPh_3)_3H$.

When the same reaction was carried out in the absence of PPh_3, the expected $Re(CO)_3(PPh_2)_2H$ was not isolated.

Single-crystal X-ray data

$C_{40}H_{33}O_4P_2Re$, $M = 825.8$, monoclinic, $a = 17.63(2)$, $b = 9.72(1)$, $c = 20.95(2)$ Å, $\beta = 104°38'(6')$, $V = 3473.2$ Å^3, $D_m = 1.57(2)$, $Z = 4$, $D_c = 1.58$ g cm^{-3}, $F(000) = 1640$. Space group $P2_1/c$, No 14. Mo-K_α radiation, $\lambda = 0.7107$ Å, μ_1(Mo-K_α) = 38.3 cm^{-1}.

Intensity measurements

A crystal with dimensions 0.21 × 0.53 × 0.21 mm was mounted on a PAILRED diffractometer and 12 levels of the reciprocal lattice, $h0l$—$h11l$, were collected within the sphere $2\theta \leqslant 50°$. 7159 diffraction intensities were measured with the ω-scan method at a scan rate 2.5° per min and background counts for 24—40 sec at the extreme points of the scan range (from 1.6—3.4°). After corrections of the intensities for Lorentz, polarization and absorption effects, a set of 2776 reflections was retained (with $I \geqslant 5\sigma(I)$) and used for structure resolution and refinement.

Determination of the structure ·

The structure was solved by the heavy atom method, but the linear geometry of the ReP_2 group and the near-zero value of the y coordinate required image duplication of the light atoms in a Fourier synthesis phased with the contribution of the rhenium and phosphorus atoms. The correct locations of the phenyl rings were found by testing structure models with the rings placed in alternative positions. A difference-Fourier synthesis, computed after refinement of the partially-solved structure, revealed light peaks of electron densities in the equatorial region. Four peaks belonged to two carbonyl groups in cis positions, while the planar and triangular geometry of the other four, strongly suggested the presence of a chelating acetate group. This structure model was successfully refined by the least-squares method down to discrepancy indexes $R = 0.035$ and $R_w = 0.038$. The presence of the acetate group was subsequently confirmed and explained as reported in the next section.

The refinement was carried out using the block-diagonal approximation of the normal matrix by rigid body treatment of the phenyl rings (C—C = 1.392, C—H = 1.08 Å, $\angle$C—C—C = C—C—H = 120°) and with individual isotropic thermal factors for the carbon atoms. In the three final cycles the full matrix was adopted and the observations were weighted according to the formula $W = 1/(A + BF_0 + CF_0^2)$ with $A = 11.6$, $B = 0.03$ and $C = 0.0001$.

Atomic scattering factors were taken from ref. 3 for Re, P, O and C and from ref. 4 for H. The rhenium and phosphorus scattering curves were corrected for both the real and imaginary parts of the anomalous dispersions [5].
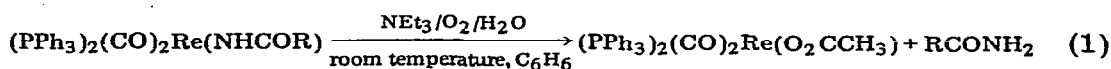
A final difference-Fourier showed residual fluctuations in the range ± 0.6 e$^-$/Å^3 and a peak for 1.5 e$^-$/Å^3 in relation to the metal atom. The structure parameters are reported in Table 2, the list of observed and computed structure factors can be obtained on application to the authors.

Computations

All computations were carried out on a UNIVAC 1106 computer. Absorption correction [6], counter data reduction and statistical analysis for weighting schemes were based upon Fortran programmes written in our laboratory. In addition, local versions of entries Nos. 7528, 7531 and 7532 and 7535 in the 1966 "International World List of Crystallographic Programs" were used for Fourier analysis, structure factor and least-squares calculations. Johnson's ORTEP was used for plotting, and a programme by Gramaccioli for computation of the molecular parameters.

Results and discussion

On treating $(PPh_3)_2(CO)_2Re(NHCOR)$ (R = C$_6$H$_5$ or p-MeC$_6$H$_4$) with NEt$_3$ and water under an atmosphere of nitrogen, no reaction occurs. However when the same reaction is carried out in the presence of traces of air, a white product is slowly formed; it does not contain the organic moiety NHCOR, which is recovered as the corresponding amide, RCONH$_2$. When the same reaction is carried out in air, it proceeds rapidly. Repeated oxygen analyses always give a ratio Re : O = 1 : 4, while in its IR spectrum the white compound does not show any significant band other than two absorptions at 1930 and 1850 cm^{-1}, assignable to terminal carbonyl groups, and the usual bands arising from the phosphine ligands. Moreover, in its ^{1}H NMR spectrum, the product shows a signal at τ 9.5 ppm which can not easily be assigned. In order to clarify the nature of this derivative, we carried out an X-ray structural determination, which surprisingly shows it to be the acetatobis(triphenylphosphine)dicarbonylrhenium(I), $(PPh_3)_2(CO)_2Re(O_2CCH_3)$, having the bulky phosphines in the *trans* positions. Thus, an oxidation of the ethyl group of the tertiary amine must be involved in generating the acetate ligand. This oxidation, which requires strong oxidising agents in the absence of metal substrates [7], proceeds under very mild conditions, according to eq. 1.

$$(PPh_3)_2(CO)_2Re(NHCOR) \xrightarrow[\text{room temperature, } C_6H_6]{NEt_3/O_2/H_2O} (PPh_3)_2(CO)_2Re(O_2CCH_3) + RCONH_2 \quad (1)$$

(R = C$_6$H$_5$ or p-MeC$_6$H$_4$)

TABLE 2 [a,b]

POSITIONAL AND THERMAL PARAMETERS OF THE ATOMS OF $(PPh_3)_2(CO)_2Re(O_2CCH_3)$

Non-group atoms [c]

Atom	x/a	y/b	z/c	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Re	2601(0)	−22(1)	2496(0)	22(0)	−4(1)	6(0)	62(0)	−9(0)	14(0)
P(1)	1510(1)	−129(4)	1528(1)	25(0)	−9(4)	8(1)	66(3)	−2(4)	14(0)
P(2)	3647(1)	176(4)	3488(1)	22(0)	2(3)	6(1)	83(4)	−13(3)	17(0)
C(1)	3285(6)	−604(12)	1994(5)	33(4)	−19(12)	12(6)	86(13)	−16(11)	17(3)
O(1)	3704(5)	−925(12)	1679(4)	46(4)	0(13)	39(5)	210(17)	−47(12)	27(3)
C(2)	2533(6)	−1842(14)	2691(7)	17(4)	8(12)	−8(6)	84(18)	−54(13)	28(4)
O(2)	2482(6)	−3006(10)	2869(5)	58(5)	−18(12)	10(6)	84(13)	−2(11)	34(3)
O(3)	1912(4)	1248(8)	3038(3)	38(3)	23(9)	16(4)	89(11)	−8(8)	15(2)
O(4)	2477(5)	2213(10)	2352(4)	46(4)	−9(10)	16(5)	93(13)	0(9)	20(3)
C(3)	2049(8)	2331(15)	2739(6)	43(6)	13(18)	−7(7)	100(18)	−6(13)	16(3)
C(4)	1685(11)	3678(17)	2845(8)	106(11)	87(24)	55(12)	115(23)	−2(17)	31(5)

Phenyl group atoms[d]

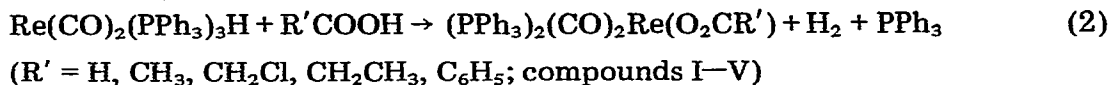| Atom	x/a	y/b	z/c	B(Å²)	Atom	x/a	y/b	z/c	B(Å²)
C(111)	1712(5)	583(9)	785(3)	3.0(2)	C(234)	4145(15)	4609(8)	4249(5)	8.0(4)
C(112)	2064(4)	1874(8)	830(3)	4.4(2)	C(235)	4032(7)	3589(10)	4682(3)	6.6(3)
C(113)	2214(5)	2478(7)	272(4)	5.5(3)	C(236)	3893(10)	2238(10)	4644(4)	4.2(2)
C(114)	2012(5)	1793(9)	−330(3)	5.1(3)	H(112)	2222	2409	1300	4.4
C(115)	1661(4)	502(8)	−374(3)	5.0(3)	H(113)	2489	3484	307	5.5
C(116)	1511(5)	−102(7)	183(4)	4.4(2)	H(114)	2129	2264	−764	5.1
C(121)	613(6)	815(16)	1576(4)	2.9(2)	H(115)	1504	−31	−843	5.0
C(122)	236(4)	1734(12)	1089(3)	4.5(2)	H(116)	1237	−1107	148	4.4
C(123)	−420(6)	2453(10)	1160(3)	5.5(3)	H(122)	454	1890	655	4.5
C(124)	−699(6)	2252(16)	1718(4)	5.0(3)	H(123)	−713	3169	782	5.5
C(125)	−321(4)	1333(12)	2205(3)	5.3(3)	H(124)	−1209	2812	1774	5.0
C(126)	334(6)	615(10)	2134(3)	4.0(2)	H(125)	−538	1178	2640	5.3
C(131)	1147(5)	−1852(7)	1268(4)	3.6(2)	H(126)	629	−100	2514	4.0
C(132)	350(4)	−2113(8)	1028(5)	5.5(3)	H(132)	−70	−1292	1009	5.5
C(133)	94(3)	−3429(9)	814(4)	6.4(3)	H(133)	−526	−3632	627	6.4
C(134)	635(5)	−4482(7)	839(4)	6.1(3)	H(134)	436	−5506	672	6.1
C(135)	1433(4)	−4221(8)	1079(5)	5.5(3)	H(135)	1855	−5041	1099	5.5
C(136)	1689(3)	−2905(9)	1293(4)	4.3(2)	H(136)	2311	−2701	1481	4.3
C(211)	4588(4)	−479(10)	3419(5)	3.6(2)	H(212)	4102	−2514	3247	5.1
C(212)	4619(4)	−1882(10)	3293(5)	5.1(3)	H(213)	5339	−3665	3131	6.8
C(213)	5314(6)	−2473(7)	3228(5)	6.8(4)	H(214)	6521	−2121	3238	7.6
C(214)	5979(4)	−1661(10)	3288(5)	7.6(4)	H(215)	6466	373	3460	7.9
C(215)	5948(4)	−258(10)	3413(5)	7.9(4)	H(216)	5229	1424	3577	5.9
C(216)	5252(6)	331(7)	3479(5)	5.9(3)	H(222)	4655	−1457	4577	4.0
C(221)	3469(5)	−765(10)	4187(4)	3.6(2)	H(223)	4341	−2792	5484	5.4
C(222)	4058(3)	−1483(11)	4629(4)	4.0(2)	H(224)	2980	−2850	5604	5.8
C(223)	3882(4)	−2234(9)	5139(4)	5.4(3)	H(225)	1932	−1573	4817	5.6
C(224)	3117(5)	−2266(10)	5207(4)	5.8(3)	H(226)	2246	−237	3910	4.7
C(225)	2528(3)	−1548(11)	4764(4)	5.6(3)	H(232)	3963	2668	2873	6.2
C(226)	2704(4)	−797(9)	4254(4)	4.7(2)	H(233)	4210	5071	3261	8.1
C(231)	3868(15)	1906(8)	3813(5)	3.4(2)	H(234)	4254	5662	4420	8.0
C(232)	3982(7)	2926(10)	3380(3)	6.2(3)	H(235)	4051	3848	5190	6.6
C(233)	4121(10)	4277(10)	3598(4)	8.1(4)	H(236)	3805	1444	4802	4.2

[a] All values × 10⁴ except for isotropic thermal parameters. [b] The numbers in parentheses here and in the subsequent Tables are the esd's on last significant digits.
[c] The b_{ij} are the coefficients of the form: $h^2 b_{11} + k^2 b_{22} + l^2 b_{33} + hk b_{12} + hl b_{13} + kl b_{23}$. [d] Hydrogen atoms have the same numbers and the same thermal parameters as the carbon atoms to which they are bonded.

Gas chromatographic analyses carried out on the mother liquor of reaction 1, show the presence of traces of acetaldehyde, while the fate of the oxidized NEt_3 has not been clarified.

The spectroscopic properties of the acetate derivative (see above) are rather peculiar. The absence of surely assignable bands due to the acetate moiety in its IR spectrum, does not allow any speculation about the possible nature of the product obtained from reaction 1. Moreover, the origin of the acetate ligand was itself unpredictable. Once the real nature of the reaction product was known, we were able to compare our results with those of the known manganese analogue, $(PPh_3)_2(CO)_2Mn(O_2CCH_3)$, the correct formulation of which also required X-ray structure determination [8]. The same spectroscopic anomalies have been noted for the manganese species, although the X-ray parameters for both the rhenium (see later) and manganese [8] compounds are entirely normal.

The high field shift of the methyl resonance for $(PPh_3)_2(CO)_2Re(O_2CCH_3)$ in its ^1H NMR spectrum is not easily explainable, although this behaviour has been already observed for other chelated acetate derivatives [9]. Shielding effects due to ring currents from the phenyl rings of the phosphines proximate to the acetate ligand have been invoked in the case of the manganese analogue [8] in order to explain this anomalous chemical shift.

The rhenium(I) acetate derivative and a series of carboxylato complexes, $(PPh_3)_2(CO)_2Re(O_2CR')$, have been obtained according to eq. 2.

$$Re(CO)_2(PPh_3)_3H + R'COOH \rightarrow (PPh_3)_2(CO)_2Re(O_2CR') + H_2 + PPh_3 \qquad (2)$$

$(R' = H, CH_3, CH_2Cl, CH_2CH_3, C_6H_5;$ compounds I—V)

Compound III ($R' = CH_2Cl$) has also been obtained by the exchange reaction of II ($R' = CH_3$) with chloroacetic acid. The acetate derivative was shown to be identical to the product discussed above. We also formulate the carboxylato derivatives (I. III—V) as having a chelated carboxylato group on the basis of their IR data, which in these cases are diagnostic (Table 3). The terminal carbonyl stretching absorptions are practically insensitive to the nature of the R' groups, however they lie at low frequencies even in III ($R' = CH_2Cl$) which has the most
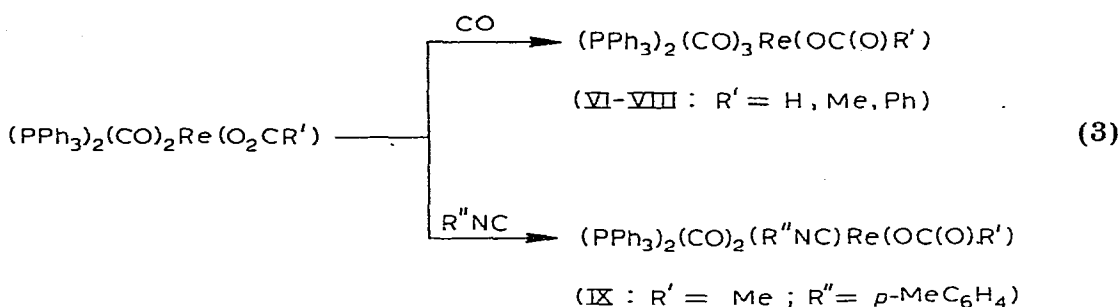
TABLE 3

IR [a] AND ^1H NMR SPECTRAL DATA

Compound	$\nu(CO)$	$\nu_{as}(OCO)$ [b]	$\nu_s(OCO)$	τ Me (ppm)
I	1930s, 1850s	1550ms	1360m	
II	1930s, 1850s	1515w		9.5 ($CDCl_3$)
III	1930s, 1850s	1640ms	1440m	c
IV	1930s, 1850s	1515m	1450m	
V	1930s, 1850s	1505ms	1440m	
VI	2040m, 1950s, 1900s	1620s	1300ms	
VII	2040m, 1940s, 1880s	1600ms	1375ms	8.56 (C_6D_6)
VIII	2030m, 1945s, 1885s	1605m	1355s	
IX [d]	1930s, 1860s	1610ms	1375ms	8.73 [e] ($CDCl_3$)
X	2040m, 1950s, 1895s	1680m	1410w	

[a] Nujol and hexachlorobutadiene mulls (cm^{-1}). [b] For the unidentate carboxylato ligand, the first value is assigned to $\nu(C=O)$ and the latter to $\nu(C-O)$. [c] $\tau(CH_2) = 7.66$ ($CDCl_3$) ppm. [d] $\nu(NC) = 2100$ cm^{-1}. [e] $\tau(Me)$ in p-$MeC_6H_4NC = 7.73$ ppm.

electronegative group of the series; this fact seems to suggest that the amount of π-back donation from the metal to the carbonyl ligands has reached a maximum, irrespective of the nature of R'. The carboxylato moiety gives rise in these compounds to IR absorptions, which are at the expected frequencies for this type of coordination [9].

The reactivity of some of the isolated carboxylato complexes have also been studied, in particular towards neutral ligands such as carbon monoxide and p-tolyl isocyanide, as indicated in eq. 3. These reactions readily cause the opening of the chelated carboxylato groups, leading to the corresponding hexacoordi-

$$
(PPh_3)_2(CO)_2Re(O_2CR') \longrightarrow \begin{array}{l} \xrightarrow{CO} (PPh_3)_2(CO)_3Re(OC(O)R') \\[4pt] \quad (VI-VIII: \ R' = H, Me, Ph) \\[20pt] \xrightarrow{R''NC} (PPh_3)_2(CO)_2(R''NC)Re(OC(O)R') \\[4pt] \quad (IX: \ R' = Me; \ R'' = p\text{-}MeC_6H_4) \end{array} \tag{3}
$$

nated derivatives (Table 1) having monodentate carboxylato ligands. For R' = Me, the reaction with carbon monoxide has been shown to be reversible; compound VII in fact looses CO when in solution, even at room temperature, it being stable only in the presence of free carbon monoxide.

A compound formulated as VIII has already been reported [10]. It has been obtained by a more complex route but the reported infrared data ($\nu(CO) = 2032s$, 1952s, 1892s; $\nu(C=O) = 1635m$; $\nu(C-O) = 1335s$ cm^{-1} in KBr) are quite different from those observed for VIII (Table 3) and this fact seems to suggest that they are isomers. The spectroscopic properties of compounds VI—IX are fully consistent with their formulations (Table 3). The asymmetric $\nu(C=O)$ is markedly shifted to high frequencies with respect to the parent chelated compounds by about 70—100 cm^{-1}, as expected [9]. Moreover, the $\Delta\nu$ between the asymmetric and symmetric absorptions of the carboxylato ligand are larger than in the parent chelated derivatives, again in agreement with what is generally reported for this type of compound. The vibrations originating from the terminal carbonyl groups in compounds (VI—VIII) (Table 3) are consistent with configurations having the two phosphine ligands in the *trans* positions and the three CO groups together with the monodentate carboxylato moiety in the equatorial plane. The positions and the intensities of the stretching bands are in fact comparable with those of related carboalkoxorhenium(I) derivatives [11]. Re(CO)$_2$-(PPh$_3$)$_3$H was allowed to react also with trifluoroacetic acid, i.e., with a carboxylic acid having the strong electron-withdrawing group CF$_3$. However, the expected (PPh$_3$)$_2$(CO)$_2$Re(O$_2$CCF$_3$) was not isolated, on the contrary, the hexacoordinated tricarbonyl derivative (PPh$_3$)$_2$(CO)$_3$Re(OC(O)CF$_3$) (X) was formed in low yields. Compound X showed a $\nu(CO)$ pattern typical for derivatives having a configuration as described for compounds VI—VIII [11]; the $\nu(C=O)$ was observed at 1680 cm^{-1} (Table 3).

General description of the crystal and molecular structure of the derivative (II)

The crystal contains discrete (PPh$_3$)$_2$(CO)$_2$Re(O$_2$CCH$_3$) molecules in which the rhenium atom is octahedrally coordinated with the phosphines in the *trans* positions; the carbonyl groups and the chelating acetate ion lie in the equatorial plane. A drawing of the molecule is presented in Fig. 1 and the coordination in the equatorial plane is depicted in Fig. 2; the idealized symmetry is C_{2v}. The molecule is stereochemically very similar to two other known structures, (PPh$_3$)$_2$-(CO)$_2$Re(S$_2$CH) [12] and (PPh$_3$)$_2$(CO)$_2$Mn(O$_2$CCH$_3$) [8]. A comparison of the bonding parameters in the three structures will be of interest.

The Re—P interactions are equal within experimental error with a mean value of 2.415 Å, which is strictly comparable with the values of other rhenium(I)—phosphine interactions: 2.418 Å in (PPh$_3$)$_2$(CO)$_2$Re(S$_2$CH) [12], 2.422 Å in ReCl(N$_2$)(PMe$_2$Ph)$_4$ [13] and 2.390 Å for the two mutually *trans* Re—P interactions in ReH$_2$(NO)(PPh$_3$)$_3$ [14]. It is also useful to compare the Re—P interactions with the corresponding value in the manganese analogue [8] (2.267 Å).

The Re—C and C—O distances are not geometrically equivalent but the differences in bond parameters can be considered packing effects, the mean values 1.85 and 1.17 Å respectively being comparable with those found in (PPh$_3$)$_2$-
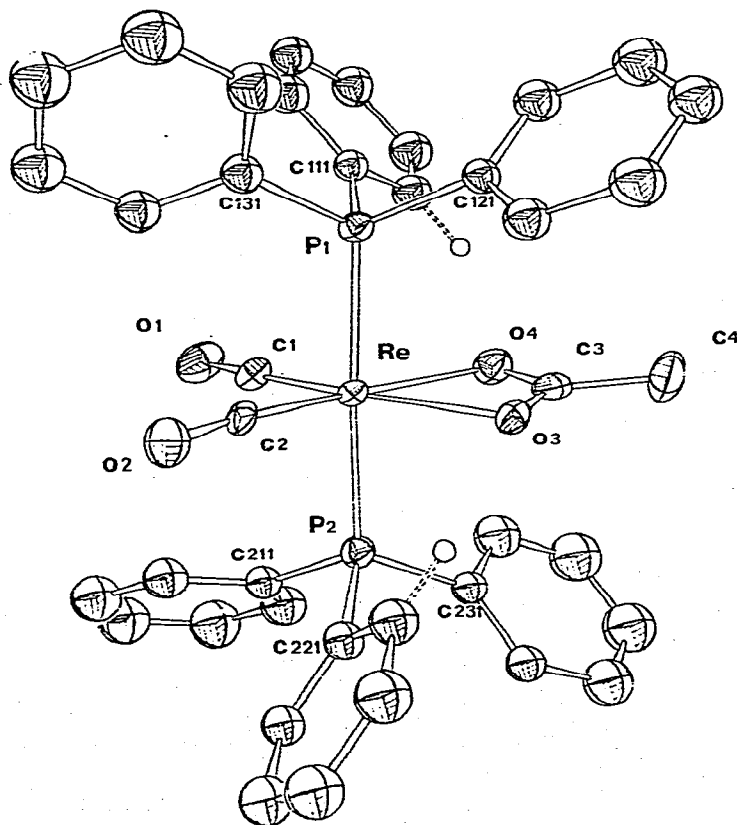

Fig. 1. Perspective view of the molecule (PPh$_3$)$_2$(CO)$_2$Re(O$_2$CCH$_3$). The thermal ellipsoids have been drawn at 30% probability.
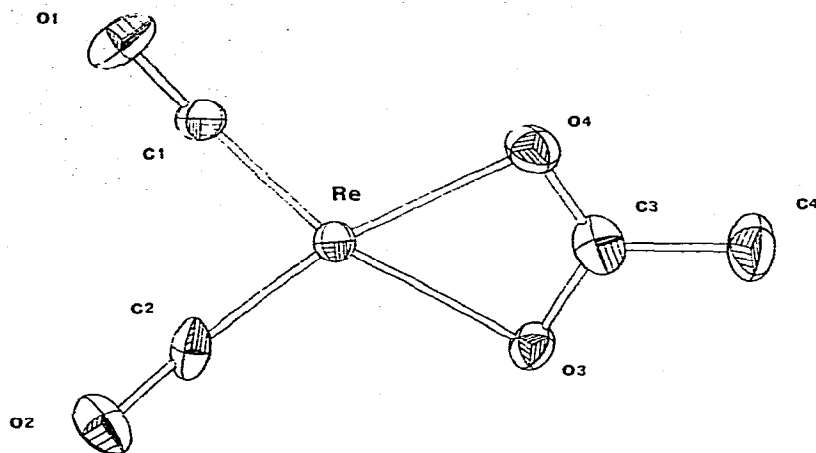
Fig. 2. A view of the moiety $(CO)_2Re(O_2CCH)_3$. Thermal ellipsoids at 30% probability.

$(CO)_2Re(S_2CH)$ (1.91 and 1.14 Å). The differences clearly indicate that in the acetate derivative the degree of π metal–carbonyl back-bonding is higher than in the dithioformate analogue, probably because the latter ligand can compete more efficiently than the former in this type of interaction. The mean Mn–C

TABLE 4

BOND DISTANCES (Å) AND RELEVANT ANGLES (°) IN $(PPh_3)_2(CO)_2Re(O_2CCH_3)$.

Re—P(1)	2.419(2)	P(2)—Re—C(2)	87.9(4)
Re—P(2)	2.412(2)	P(1)—Re—O(3)	91.8(3)
Re—O(3)	2.23(1)	P(2)—Re—O(3)	85.1(3)
Re—O(4)	2.20(1)	P(1)—Re—O(4)	84.1(3)
Re—C(1)	1.88(1)	P(2)—Re—O(4)	93.8(3)
Re—C(2)	1.83(1)	C(1)—Re—C(2)	85.5(6)
Re—C(3)	2.59(2)	C(2)—Re—O(3)	110.4(5)
C(1)—O(1)	1.15(2)	O(3)—Re—O(4)	58.3(3)
C(2)—O(2)	1.20(2)	O(4)—Re—C(1)	106.0(5)
C(3)—O(3)	1.28(2)	Re—O(3)—C(3)	90.8(8)
C(3)—O(4)	1.25(2)	Re—O(4)—C(3)	93.3(9)
C(3)—C(4)	1.50(2)	O(3)—C(3)—C(4)	120(1)
O(3) ⋯ O(4)	2.16(1)	O(4)—C(3)—C(4)	122(1)
P(1)—C(111)	1.82(1)	O(3)—C(3)—O(4)	118(1)
P(1)—C(121)	1.85(1)	Re—C(1)—O(1)	178(1)
P(1)—C(131)	1.83(1)	Re—C(2)—O(2)	175(1)
P(2)—C(211)	1.82(1)	Re—P(1)—C(111)	114.5(3)
P(2)—C(221)	1.82(1)	Re—P(1)—C(121)	116.2(3)
P(2)—C(231)	1.82(1)	Re—P(1)—C(131)	115.7(3)
O(3) ⋯ H(226)	2.29	Re—P(2)—C(211)	114.7(4)
O(4) ⋯ H(112)	2.14	Re—P(2)—C(221)	113.8(3)
P(1)—Re—P(2)	176.8(2)	Re—P(2)—C(231)	116.2(6)
P(1)—Re—C(1)	90.2(4)	C(111)—P(1)—C(121)	102.3(5)
P(2)—Re—C(1)	92.7(4)	C(121)—P(1)—C(131)	103.4(6)
P(1)—Re—C(2)	93.6(4)	C(131)—P(1)—C(111)	103.0(5)
		C(211)—P(2)—C(221)	103.5(5)
		C(221)—P(2)—C(231)	103.2(6)
		C(231)—P(2)—C(211)	103.9(9)

and C—O bond lengths in the manganese analogue are 1.73 and 1.15 Å respectively. The acetate ligand is symmetrically coordinated and possesses idealized C_{2v} symmetry. Its geometry is not significantly different from that found in the manganese analogue, as one can see by comparing the values in Table 4 with the following values found in the manganese complex: C—O 1.25(1), C—C 1.53(1) Å, O—C—O 116(1)°.

The rhenium and manganese complexes have strictly similar stereochemistries and their crystals are isomorphous. The equatorial atoms are nearly in the same plane in both crystals, the displacement from the best plane not exceeding 0.09 Å. Another feature of the manganese complex, that is, the existence of two short interactions between phenyl hydrogens and acetate oxygens (see Fig. 1 and Table 4), is also present in the rhenium analogue. The main structural differences are those due to the greater covalent radius of the rhenium atom. The Re—P and Re—O interactions differ from the corresponding Mn—P and Mn—O values by about 0.15 Å in both cases. The difference for the Re—(CO) and Mn—(CO) values is slightly lower, 0.12 Å, but that between the Re ··· O and Mn ... O distances, less dependent on the degree of interactions, is again 0.15 Å. Such a constant difference in three types of bonding interactions can be taken as a good estimate of the difference in covalent radius for the two metal atoms.

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References

1 S. Cenini and G. La Monica, Inorg. Chem. Acta Rev., (1976) in press.
2 G. La Monica, S. Cenini, F. Porta and M. Pizzotti, Proc. 7th. Int. Conf. Organometal. Chem., Venice, September 1975.
3 D.T. Cromer and J.B. Mann, Acta Crystallogr., Sect. A, 24 (1968) 321.
4 J.B. Forsyth and M. Wells, Acta Crystallogr., 12 (1959) 412.
5 International Tables for X-ray Crystallography, vol. III, Kynoch Press, Birmingham, 1962.
6 G. Ciani, M. Manassero and M. Sansoni, J. Appl. Crystallogr., 4 (1971) 173.
7 S. Patai (Ed.), The Chemistry of the amino group, Interscience, London, 1972.
8 W.K. Dean, G.L. Simon, P.M. Treichel and L.F. Dahl, J. Organometal. Chem., 50 (1973) 193.
9 S.D. Robinson and M.F. Uttley, J. Chem. Soc. Dalton Trans., (1973) 1912.
10 E. Linder and R. Grimer, J. Organometal. Chem., 31 (1971) 249.
11 T. Kruck and M. Noack, Chem. Ber., 97 (1964) 1693.
12 V.G. Albano, P.L. Bellon and G. Ciani, J. Organometal. Chem., 31 (1971) 75.
13 B.R. Davies and J.A. Ibers, Inorg. Chem., 10 (1971) 578.
14 G. Ciani, D. Giusto, M. Manassero and A. Albinati, J. Chem. Soc. Dalton Trans, in press.