Complexes with Functional Phosphines. Part 18.[1] Ruthenium Complexes and Clusters with Ketophosphine or Phosphino Enolate Ligands†

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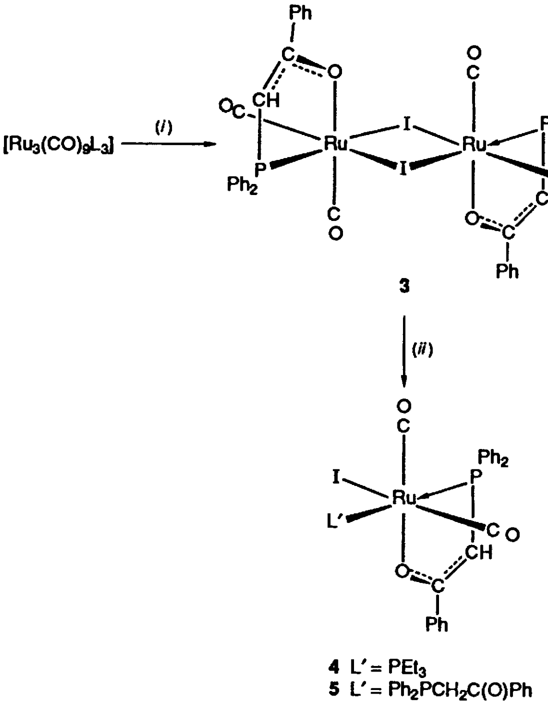
Reaction of the ketophosphine $Ph_2PCH_2C(O)Ph$ (L) with $[Ru_3(CO)_{12}]$ in tetrahydrofuran in the presence of Me_3NO affords $[Ru_3(CO)_9L_3]$ which reacts with I_2 to give $[\{Ru(\mu\text{-}I)[Ph_2PCH{\cdots}C({\cdots}O)Ph](CO)_2\}_2]$. The iodide bridges are readily cleaved by PEt_3 or L, affording the mononuclear, phosphino enolate complexes $[RuI\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}(CO)_2L']$ [L' = PEt_3 or $Ph_2PCH_2C(O)Ph$] in which the P atoms are *trans* to each other. The crystal structure of $[\{Ru(\mu\text{-}Cl)[Ph_2PCH{\cdots}C({\cdots}O)Ph](CO)_2\}_2]$ which forms slowly in CH_2Cl_2 solutions of $[Ru_3(CO)_{10}L_2]$ is determined.

Complexes with hemilabile oxygen–phosphorus ligands are of increasing interest in co-ordination chemistry and catalysis but studies of them have been mostly limited to mononuclear transition-metal complexes.[2] In view of our interest in these ligands and in the chemistry of transition-metal clusters,[3] we have recently begun a study of the reactions between functional phosphines of the type $Ph_2PCH_2C(O)Ph$ (L) and the trinuclear clusters $[Ru_3(CO)_{12}]$ and $[Fe_3(CO)_{12}]$. Whereas the cluster core of the latter is easily fragmented, we obtained earlier with the ruthenium analogue the mono- and di-substituted clusters $[Ru_3(CO)_{11}L]$ and $[Ru_3(CO)_{10}L_2]$ as well as the cluster $[Ru_3(\mu\text{-}H)\{\mu\text{-}O({\cdots}CPh){\cdots}CHPPh_2\}(CO)_9]$ which contains the phosphino enolate ligand bound in an unprecedented bridging fashion.[1] In this paper we report the synthesis and characterisation of halide-bridged diruthenium complexes containing chelating phosphino enolate ligands, derived from the trisubstituted cluster derivative $[Ru_3(CO)_9L_3]$.

Results and Discussion

Syntheses.—In the course of our investigations of the chemistry of ruthenium carbonyl clusters with the ketophosphine ligand $Ph_2PCH_2C(O)Ph$ (L) we observed that a CH_2Cl_2 solution of the disubstituted cluster $[Ru_3(CO)_{10}L_2]$ progressively yielded upon standing modest yields of the new dinuclear complex $[\{Ru(\mu\text{-}Cl)[Ph_2PCH{\cdots}C({\cdots}O)Ph](CO)_2\}_2]$ **2**. This complex was fully characterised and its molecular structure was determined by X-ray diffraction (see below). We then devised a better synthetic route to the corresponding iodo derivative $[\{Ru(\mu\text{-}I)[Ph_2PCH{\cdots}C({\cdots}O)Ph](CO)_2\}_2]$ **3** by reaction of I_2 with the red-violet cluster $[Ru_3(CO)_9\{Ph_2PCH_2C(O)Ph\}_3]$ **1** (Scheme 1), prepared from $Ph_2PCH_2C(O)Ph$ and $[Ru_3(CO)_{12}]$ (see Experimental section).



Scheme 1 (*i*) I_2, Me_2CO; (*ii*) 2L'

The spectroscopic properties of the dinuclear complexes **2** and **3** are very similar. Their ν(CO) vibrations occur around 2055 and 2000 cm^{-1}, values which are similar to those found for *e.g.* $[\{Ru(\mu\text{-}X)X(CO)_2(PPh_3)\}_2]$,[4] or for dinuclear cyclometallated ruthenium(II) complexes containing two CO ligands in *cis* position.[5] A typical ν(C${\cdots}$O) + ν(C${\cdots}$C) absorption of the phosphino enolate ligand is found around 1515 cm^{-1}.[6] Their ^1H NMR spectra contain the expected doublet around δ 5.20 for the PCH proton. In the $^{31}P\text{-}\{^1H\}$ NMR spectrum a singlet is observed around δ 50. Previous studies have shown that halogenation of triruthenium carbonyl clusters may occur with either fragmentation or retention of the cluster core.[7]

We have attempted to perform nucleophilic substitution reactions on $[\{Ru(\mu\text{-}I)[Ph_2PCH{\cdots}C({\cdots}O)Ph](CO)_2\}_2]$, using carbonylmetalates such as $[Co(CO)_4]^-$ or $[W(\eta\text{-}C_5H_5)(CO)_3]^-$. Although a reaction occurred in 1 h in tetrahydro-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

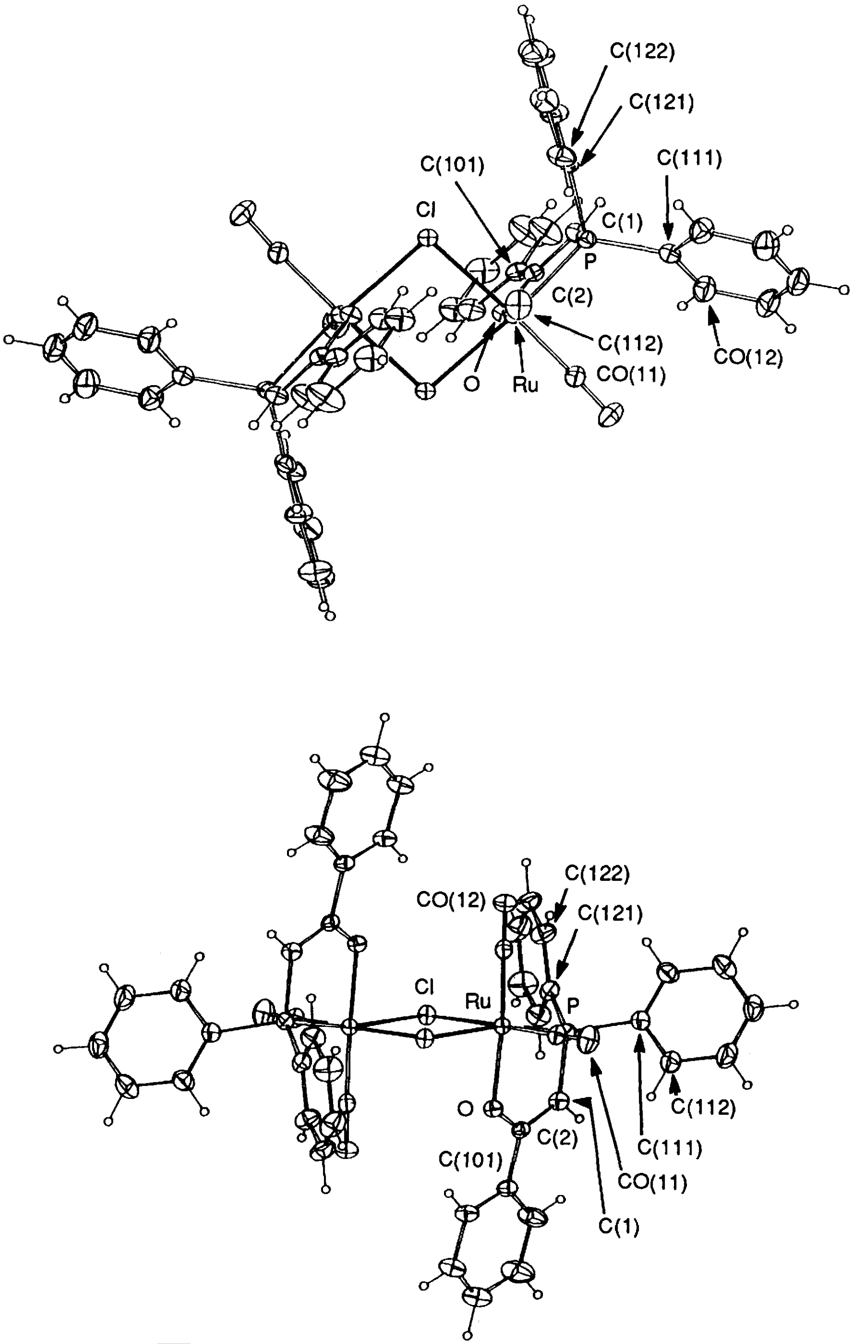

Fig. 1 Projection of a single dimer of $[\{\overline{\mathrm{Ru}(\mu\text{-}\mathrm{Cl})[\mathrm{Ph_2PCH}\overset{\cdots}{-}\mathrm{C}(\overset{\cdots}{-}\mathrm{O}})\mathrm{Ph}](\mathrm{CO})_2\}_2]$ **2** normal and oblique to the $\mathrm{Ru_2Cl_2}$ plane, showing non-hydrogen atom labelling and 20% thermal ellipsoids. Hydrogen atoms have arbitrary radii of 0.1 Å

furan (thf), unstable products or mixtures were formed which were not further investigated. However, the expected bridge-splitting reaction occurred when $[\{\overline{\mathrm{Ru}(\mu\text{-}\mathrm{I})[\mathrm{Ph_2PCH}\overset{\cdots}{-}\mathrm{C}(\overset{\cdots}{-}\mathrm{O}})\mathrm{Ph}](\mathrm{CO})_2\}_2]$ reacted with tertiary phosphines such as $\mathrm{PEt_3}$ or $\mathrm{Ph_2PCH_2C(O)Ph}$, affording the corresponding air-stable mononuclear enolato complexes $[\overline{\mathrm{RuI}\{\mathrm{Ph_2PCH}\overset{\cdots}{-}\mathrm{C}(\overset{\cdots}{-}\mathrm{O}})\mathrm{Ph}\}(\mathrm{CO})_2(\mathrm{PEt_3})]$ **4** and $[\overline{\mathrm{RuI}\{\mathrm{Ph_2PCH}\overset{\cdots}{-}\mathrm{C}(\overset{\cdots}{-}\mathrm{O}})\mathrm{Ph}\}(\mathrm{CO})_2\{\mathrm{Ph_2PCH_2C(O)Ph}\}]$ **5**, respectively, in which the P atoms are *trans* to each other [J(PP) = 276 and 296 Hz, respectively], while the CO ligands remain in *cis* position (see Experimental section).[5,8]

Attempts to form a carbon–carbon bond between the enolato carbon of complex **3** and $p\text{-MeC}_6\mathrm{H_4N{=}C{=}O}$ or $\mathrm{RC{\equiv}CR}$ ($\mathrm{R = CO_2Me}$) were unsuccessful, indicating that the reactivity of the enolate co-ordinated to Ru in these types of complexes is lower than when bound to Ni, Pd or Pt.[9] After prolonged reaction in thf, and more rapidly upon heating, a very strong absorption appeared in the IR at 1731 $\mathrm{cm^{-1}}$. When pure **3** was stirred in thf overnight at *ca.* 20 °C new absorptions developed in the IR spectrum at 1779vs, 1726m and 1718 (sh) $\mathrm{cm^{-1}}$. The same observations were made when this transformation was carried out under an atmosphere of CO, but it required a longer reaction time (*ca.* 4 d), indicating an inhibition effect caused by CO. In none of these reactions was metal formation observed. Evaporation of the yellow solution left an oil, which was extracted in pentane, leaving behind a yellow solid whose $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ NMR spectrum (thf–$\mathrm{C_6D_6}$) contained the resonance due to **3** (major) and two other peaks at δ 54.4 and 46.4. Evaporation of the pentane extract under reduced pressure left an oil with a characteristic smell, which has IR absorptions at 1779vs and 1726m $\mathrm{cm^{-1}}$. It contained products of

Table 1 Non-hydrogen positional parameters

Atom	*x*	*y*	*z*
Ru	0.057 60(3)	0.330 64(3)	0.536 67(1)
Cl	0.170 8(1)	0.548 8(1)	0.528 11(5)
C(11)	−0.037 2(5)	0.168 3(5)	0.540 5(2)
O(11)	−0.099 1(4)	0.071 8(4)	0.540 7(2)
C(12)	0.081 8(5)	0.260 7(5)	0.466 9(2)
O(12)	0.099 3(4)	0.221 8(4)	0.425 2(2)
P	0.272 5(1)	0.254 4(1)	0.612 41(5)
C(1)	0.269 3(4)	0.337 6(5)	0.678 1(2)
C(2)	0.149 8(4)	0.415 9(4)	0.667 2(2)
O	0.041 2(3)	0.424 2(3)	0.612 6(1)
C(111)	0.299 4(4)	0.068 7(5)	0.630 1(2)
C(112)	0.238 0(6)	0.010 5(6)	0.666 7(2)
C(113)	0.251 9(7)	−0.130 8(6)	0.680 8(3)
C(114)	0.326 0(7)	−0.214 2(6)	0.658 9(3)
C(115)	0.387 9(7)	−0.160 2(6)	0.623 1(3)
C(116)	0.375 9(6)	−0.017 8(5)	0.608 6(2)
C(121)	0.428 3(4)	0.313 9(5)	0.601 8(2)
C(122)	0.447 0(5)	0.281 9(6)	0.548 0(2)
C(123)	0.564 9(6)	0.332 8(7)	0.539 9(2)
C(124)	0.659 6(6)	0.418 2(8)	0.584 8(3)
C(125)	0.643 1(6)	0.452 6(7)	0.637 0(3)
C(126)	0.525 9(5)	0.401 3(6)	0.645 7(2)
C(101)	0.133 5(5)	0.500 0(5)	0.718 0(2)
C(102)	0.014 6(5)	0.581 6(6)	0.703 4(2)
C(103)	−0.003 5(6)	0.662 4(6)	0.747 8(3)
C(104)	0.097 0(7)	0.663 1(7)	0.807 4(3)
C(105)	0.216 2(7)	0.583 5(8)	0.823 1(3)
C(106)	0.236 3(6)	0.502 7(7)	0.778 5(2)

Table 2 Molecular core geometry: *r*/Å is the ruthenium–ligand distance; other entries are the angles (°) subtended at the ruthenium atom by the relevant atoms at the head of the row and column

Atom	*r*	C(11)	C(12)	P	O	Cl′
Cl	2.439(2)	177.2(1)	89.4(2)	89.93(5)	85.2(1)	85.01(6)
C(11)	1.851(5)		90.6(2)	92.9(1)	94.9(2)	92.2(1)
C(12)	1.881(5)			97.1(1)	174.6(2)	94.0(1)
P	2.296(1)				82.58(8)	167.70(4)
O	2.065(3)					85.83(8)
Cl′	2.480(1)					

Primed atoms lie at $\bar{x}$,1 − *y*,1 − *z*. Ru–Cl–Ru′ 94.99(6)°, Ru–C(*n*1)–O(*n*1) 177.2(4) and 177.9(4)° (*n* = 1 and 2), Ru–P–C(1,111,121) 99.7(1), 119.5(1) and 114.3(1)°, C(1)–P–C(111,121) 107.5(2) and 108.9(2)°, C(111)–P–C(121) 106.2(2)°, C(2)–O,C(1) 1.301(4) and 1.369(6) Å; ligand ring angles at O,C(1,2) are 118.5(3), 115.8(3) and 123.2(4)°.

carbonylation of thf, currently under investigation. The same carbonylation products were again found when **5** was treated with Tl[PF$_6$] in thf. The anticipated cationic complex [Ru{Ph$_2$PCH$\cdots$C($\cdots$O)Ph}(CO)$_2${Ph$_2$PCH$_2$C(O)Ph}]$^+$ containing the chelated Ph$_2$PCH$_2$C(O)Ph ligand was not observed and IR monitoring of the ν(CO) region indicated the presence of the unreacted precursor. No reaction was observed in CH$_2$Cl$_2$ (IR and ^{31}P-{^{1}H} NMR monitoring). These observations suggest that iodide abstraction is a sluggish reaction in thf which produces a small quantity of a cationic complex (not detected) that could easily co-ordinate a solvent molecule and which appears to be readily carbonylated under very mild conditions. Similarly, the dimeric structure of **3** could be broken upon dissolution in thf (see above), with formation of a catalytically active solvent complex of the type [RuI{Ph$_2$PCH$\cdots$C($\cdots$O)Ph}(CO)$_2$(thf)]. Related chloride-bridge splitting reactions of [{RuCl$_2$(CO)$_3$}$_2$] have previously been observed in thf.[10]

Molecular Structure of [{Ru(μ-Cl)[Ph$_2$PCH$\cdots$C($\cdots$O)Ph](CO)$_2$}$_2$] **2**.—The results of the single-crystal X-ray structure determination of complex **2** are consistent with the above stoichiometry, formulating the molecule as a dichloro-bridged centrosymmetric dimer (Fig. 1, Table 2). In the RuC$_2$Cl$_2$PO quasi-octahedral co-ordination environment significant non-trivial differences are observed between the bonds to the pairs of carbon and chlorine ligand atoms, consistent with the presence of differing *trans* influences of the opposed ligands. The phosphorus atoms are *trans* to the bridging chlorides and each enolato oxygen is *trans* to a carbonyl ligand. The ligand grouping C(1,2,101)O is precisely planar with Ru and P deviations of 0.195(6) and 0.087(7) Å, and substantially coplanar with the associated phenyl ring plane [interplanar dihedral angle, 2.5(2)°] and approximately normal to the Ru$_2$Cl$_2$ plane [dihedral angle 79.7(1)°]. The bonding within the chelate ring shows significant delocalisation with C(1)–C(2) lengthened to 1.369(6) Å and C(2)–O and P–C(1) shortened to 1.301(4) and 1.749(5) Å. The angle C(102)–C(101)–C(106) is reduced well below 120°.

Experimental

All reactions were performed in Schlenk-type flasks under nitrogen. Solvents were dried and distilled under nitrogen: diethyl ether and tetrahydrofuran from sodium–benzophenone; toluene, pentane and hexane from sodium; dichloromethane over P$_2$O$_5$. Nitrogen (Air liquide R-grade) was passed through BASF R3-11 catalyst and molecular sieve columns to remove residual oxygen and water. Elemental analysis (C, H and N) were performed by the Service Central de Microanalyses du CNRS. Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Perkin-Elmer 398 spectrophotometer or on a Bruker IFS instrument, ^{1}H and ^{31}P NMR spectra at 200.13 and 81.02 MHz, respectively, on a FT-Bruker WP 200 SY instrument. Chemical shifts are positive downfield relative to external SiMe$_4$ for ^{1}H and to external 85% H$_3$PO$_4$ in water for ^{31}P NMR spectra.

Preparations.—[Ru$_3$(CO)$_9${Ph$_2$PCH$_2$C(O)Ph}$_3$] **1**. Solid Ph$_2$PCH$_2$C(O)Ph (0.713 g, 2.346 mmol) was added to a stirred solution of [Ru$_3$(CO)$_{12}$] (0.500 g, 0.782 mmol) in thf (100 cm^3) and the flask was placed in a cold bath at −78 °C. A solution of Me$_3$NO (0.175 g, 2.333 mmol) in thf (10 cm^3) was then added to the stirred solution over a period of 15 min. The temperature was allowed to raise to ambient and this was accompanied by a colour change from orange to red-violet. The solvent was evaporated under reduced pressure and the residue was chromatographed on silica gel. Elution with toluene gave a minor, yellow fraction that was not identified. Elution with CH$_2$Cl$_2$ afforded a red fraction which was recrystallised from CH$_2$Cl$_2$–pentane at −20 °C, yielding red-violet, air-stable microcrystals of complex **1** (0.912 g, 79% yield). IR: ν(CO) (thf) 2043w, 1979s and 1969s, ν(C=O) (KBr) 1682m and 1672m cm^{-1}. NMR (CDCl$_3$): ^{1}H, δ 4.23 [d, 6 H, PCH$_2$, ^2J(PH) 7.73 Hz] and 7.21–7.64 (m, 45 H, aromatic); ^{31}P-{^{1}H}, δ 23.6 (s) [Found: C, 56.20; H, 3.45. Calc. for C$_{69}$H$_{51}$O$_{12}$P$_3$Ru$_3$ (*M* = 1466.97): C, 56.45; H, 3.45%]. Mass spectrum (fast atom bombardment, FAB): *m*/*z* 1469 (M^+).

[{Ru(μ-Cl)[Ph$_2$PCH$\cdots$C($\cdots$O)Ph](CO)$_2$}$_2$] **2**. A solution of [Ru$_3$(CO)$_{10}${Ph$_2$PCH$_2$C(O)Ph}$_2$][1] (0.077 g, 0.064 mmol) was stirred in CH$_2$Cl$_2$ (10 cm^3) for 1 week. The colour progressively changed from red to yellow. Addition of pentane (20 cm^3) induced precipitation of the product as a yellow powder (0.025 g, 39% yield), which was recrystallised by slow diffusion of pentane into a CH$_2$Cl$_2$ solution. IR: ν(CO) (CHCl$_3$) 2091w, 2061s and 2001s; ν(C$\cdots$O) + ν(C$\cdots$C) (KBr) 1516s cm^{-1}. NMR (CDCl$_3$): ^{1}H, δ 5.20 [d, 2 H, PCH, ^2J(PH) 4.5 Hz] and 7.26–8.19 (m, 30 H, aromatic); ^{31}P-{^{1}H}, δ 52.5 (s) [Found: C, 53.05; H, 3.15. Calc. for C$_{44}$H$_{32}$Cl$_2$O$_6$P$_2$Ru$_2$ (*M* = 993.14): C, 53.15; H, 3.20%].

$[\{\overline{\mathrm{Ru}(\mu\text{-I})[\mathrm{Ph_2PCH}\overset{\cdots}{-}\mathrm{C}(\overset{\cdots}{-}\mathrm{O}})\mathrm{Ph}](\mathrm{CO})_2\}_2]$ **3**. A solution of I_2 (0.079 g, 0.311 mmol) in acetone (5 cm^3) was slowly added at 30 °C to a solution of $[\mathrm{Ru_3(CO)_9\{Ph_2PCH_2C(O)Ph\}_3}]$ (0.320 g, 0.218 mmol) in acetone (15 cm^3). After being stirred for 60 h the dark red solution gave a yellow precipitate of the product which was filtered off and recrystallised from CH_2Cl_2–hexane (0.291 g, 76% yield). IR: ν(CO) (CH_2Cl_2) 2052s and 1995s; ν(C$\overset{\cdots}{-}$O) + ν(C$\overset{\cdots}{-}$C) (KBr) 1512s cm^{-1}. NMR: ^{1}H (CD_2Cl_2), δ 5.18 [d, 2 H, PCH, ^2J(PH) 4.0 Hz] and 7.44–8.17 (m, 30 H, aromatic); ^{31}P-{^{1}H} ($CDCl_3$), δ 50.4 (s) [Found: C, 45.10; H, 2.80. Calc. for $C_{44}H_{32}I_2O_6P_2Ru_2$ (M = 1173.7): C, 45.00; H, 2.70%].

$[\overline{\mathrm{RuI}\{\mathrm{Ph_2PCH}\overset{\cdots}{-}\mathrm{C}(\overset{\cdots}{-}\mathrm{O}})\mathrm{Ph}\}(\mathrm{CO})_2(\mathrm{PEt_3})]$ **4**. Pure PEt_3 (0.022 cm^3, 0.148 mmol) was added dropwise to a solution of $[\{\overline{\mathrm{Ru}(\mu\text{-I})[\mathrm{Ph_2PCH}\overset{\cdots}{-}\mathrm{C}(\overset{\cdots}{-}\mathrm{O}})\mathrm{Ph}](\mathrm{CO})_2\}_2]$ (0.085 g, 0.072 mmol) in thf (30 cm^3). The reaction mixture was maintained at 50 °C for 1 h. The solvent was removed under reduced pressure and the residue was washed with pentane, affording complex **4** as a pale yellow powder (0.055 g, 54% yield). IR (thf): ν(CO) 2036s and 1973s; ν(C$\overset{\cdots}{-}$O) + ν(C$\overset{\cdots}{-}$C) 1517m cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 1.24 [dt, 9 H, CH_3, ^{3+5}J(PH) 15.3, J(HH) 7.5], 2.29 [dq, 6 H, CH_2, ^{2+4}J(PH) 7.3, J(HH) 7.5], 5.37 [br s, 1 H, PCH, ^2J(PH) < 1 Hz] and 7.26–7.87 (m, 15 H, aromatic); ^{31}P-{^{1}H}, δ 17.8 [d, ^2J(PP) 276, PEt_3] and 33.8 [d, ^2J(PP) 277 Hz, Ph_2PCH] [Found: C, 47.20; H, 4.35. Calc. for $C_{28}H_{31}IO_3P_2Ru$ (M = 705.01): C, 47.65; H, 4.40%].

$[\overline{\mathrm{RuI}\{\mathrm{Ph_2PCH}\overset{\cdots}{-}\mathrm{C}(\overset{\cdots}{-}\mathrm{O}})\mathrm{Ph}\}(\mathrm{CO})_2\{\mathrm{Ph_2PCH_2C(O)Ph}\}]$ **5**. This complex was prepared in a manner similar to that of the PEt_3 derivative, but starting from $Ph_2PCH_2C(O)Ph$ (0.045 g) and a reaction time of 2 h. A light yellow powder was obtained (75% yield). IR: (CH_2Cl_2) ν(CO) 2048s and 1987s; ν(C=O) 1675mw, ν(C$\overset{\cdots}{-}$O) + ν(C$\overset{\cdots}{-}$C) 1518m; (KBr) ν(CO) 2042s and 1981s; ν(C=O) 1675mw, ν(C$\overset{\cdots}{-}$O) + ν(C$\overset{\cdots}{-}$C) 1517m cm^{-1}. NMR: ^{1}H ($CDCl_3$), δ 5.04 ['t', 2 H, PCH_2, ^{2+4}J(PH) 18.1], 5.43 [dd, 1 H, PCH, J(PH) 2.4, 2.1 Hz] and 7.17–7.93 (m, 30 H, aromatic); ^{31}P-{^{1}H} (thf–C_6D_6), δ 16.8 [d, ^2J(PP) 295.8, Ph_2PCH_2] and 36.7 [d, ^2J(PP) 295.7 Hz, Ph_2PCH] [Found: C, 57.35; H, 4.15. Calc. for $C_{42}H_{33}IO_4P_2Ru$ (M = 890.75): C, 56.60; H, 4.15%].

X-Ray Data Collection and Structure Determination of $[\{\overline{\mathrm{Ru}(\mu\text{-Cl})[\mathrm{Ph_2PCH}\overset{\cdots}{-}\mathrm{C}(\overset{\cdots}{-}\mathrm{O}})\mathrm{Ph}](\mathrm{CO})_2\}_2]$ **2**.—Crystals were obtained by slow recrystallisation from CH_2Cl_2–hexane. A crystal of approximate dimensions 0.22 × 0.37 × 0.15 mm was used for the X-ray analysis.

Crystal data. $C_{44}H_{32}Cl_2O_6P_2Ru_2$, M = 991.7, monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), a = 10.286(2), b = 9.568(11), c = 23.495(4) Å, β = 114.93(1)°, U = 2097(2) Å^3, Z = 2 dimers, D_c = 1.57 g cm^{-3}, F(000) = 992, μ_{Mo} = 8.7 cm^{-1}, $A^*_{min,max}$ = 1.12, 1.33.

Data collection and structure solution. A unique diffractometer data set was measured at *ca.* 295 K [Enraf–Nonius CAD-4 machine, monochromatic Mo-Kα radiation ($\lambda = 0.7107_3$ Å), conventional 2θ–θ scan mode] yielding 3680 independent reflections, 2904 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x,y,z,U_{iso})_H$ were included constrained at estimated values. Conventional residuals on $|F|$ at convergence were R = 0.033, R' = 0.037 [statistical weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$]. Neutral-atom complex scattering factors were employed;[11] computation used the XTAL 3.0 program system,[12] implemented by S. R. Hall. Pertinent results are given in Fig. 1 and Tables 1 and 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

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