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STABILISATION OF $[Fe_2(CO)_9]$ AND $[Ru_2(CO)_9]$ BY SUBSTITUTION WITH BRIDGING DIPHOSPHORUS LIGANDS

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Summary

Reaction of $[Fe_2(CO)_9]$ with a half molar amount of R_2PYPR_2 ($Y = CH_2$, $R = Ph$, Me, OMe or OPr^i; $Y = N(Et)$, $R = OPh$, OMe or OCH_2; $Y = N(Me)$, $R = OPr^i$ or OEt) leads to the ready formation of a product which on irradiation with ultraviolet light rapidly decarbonylates to the heptacarbonyl derivative $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}R_2PYPR_2\}]$. Treatment of the latter with a slight excess of the appropriate ligand results, under photochemical conditions, in the formation of the dinuclear pentacarbonyl complex $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}R_2PYPR_2\}_2]$ but under thermal conditions in the formation of the mononuclear species $[Fe(CO)_3\{R_2PYPR_2\}]$. Reaction of $[Ru_3(CO)_{12}]$ with an equimolar amount of $(RO)_2PN(R')P(OR)_2$ ($R' =$ Me, $R = Pr^i$ or Et; $R' =$ Et, $R =$ Ph or Me) under either thermal or photochemical conditions produces $[Ru_3(CO)_{10}\{\mu\text{-}(RO)_2PN(R')P(OR)_2\}]$ which reacts further with excess $(RO)_2PN(R')P(OR)_2$ on irradiation with ultraviolet light to afford the dinuclear compound $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PN(R')P(OR)_2\}_2]$. The molecular structure of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$, which has been determined by X-ray crystallography, is described.

Introduction

Although $[Fe_2(CO)_9]$ can be readily synthesised in high yield by irradiation of $[Fe(CO)_5]$ with ultraviolet light in an appropriate solvent [1], it is unstable in solution degrading to $[Fe(CO)_5]$ and $[Fe(CO)_4]$ or $[Fe(CO)_4(solvent)]$ [2]; its ease of preparation relies on its limited solubility in most solvents [1]. $[Ru_2(CO)_9]$ is

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similarly very unstable in solution and in fact, has only been detected transiently in the photolysis of $[Ru(CO)_5]$ at temperatures of −40 °C and less [3]. Group V bidentate ligands of the type $R_2PnYPnR_2$ (R = alkyl, aryl, alkoxy group, etc; Pn = P, As, etc; Y = O, NR′, CH_2, etc; R′ = alkyl group) in which the donor atoms are linked through a single atom are excellent bridging ligands with their tendency to bridge increasing along the series $CH_2 < NR' < O$. We are utilizing phosphorus ligands of this type to stabilize unusual di-, tri- and poly-nuclear compounds and have previously established that $[Fe_2(CO)_9]$ can indeed be stabilized by substitution with the pyrophosphite $(EtO)_2POP(OEt)_2$ and in particular that reaction of diiron nonacarbonyl with this ligand leads to the formation of $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}(EtO)_2POP(OEt)_2\}]$ and $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(EtO)_2POP(OEt)_2\}_2]$ [4]. Similar observations were made by Cotton et al. who utilised $Ph_2PCH_2PPh_2$ to synthesise $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}Ph_2PCH_2PPh_2\}]$ [5] and by King et al. who synthesised $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}F_2PN(Me)PF_2\}]$ and $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}F_2PN(Me)PF_2\}_2]$ by treatment of $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$ respectively with $F_2PN(Me)PF_2$ under appropriate reaction conditions [6]. It has now been established that the diphosphazane ligands $(RO)_2PN(R')P(OR)_2$ (R′ = Et, R = Ph, Me, or CH_2; R′ = Me, R = Et or Pr^i) and the ditertiary phosphine and phosphite ligands $R_2PCH_2PR_2$ (R = Ph, Me, OPr^i or OMe) afford not only stable bis- and tetra-substituted derivatives of $[Fe_2(CO)_9]$ but also stable tetrasubstituted derivatives of $[Ru_2(CO)_9]$. The results of this investigation are reported here *.

Results and discussion

Treatment of a suspension of $[Fe_2(CO)_9]$ in toluene with a half molar amount of R_2PYPR_2 (Y = CH_2, R = Me, Ph, OPr^i or OMe; Y = N(Et), R = OPh or OMe; Y = N(Me), R = OPr^i or OEt) was found to afford reaction mixtures whose infrared spectra exhibited C–O stretching peaks of frequency and band pattern consistent with the formation of $[Fe_2(CO)_8\{\mu\text{-}R_2PYPR_2\}]$ (e.g. $[Fe_2(CO)_8\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}]$: ν(C–O) 2060m, 1988m, 1953s,br and 1945sh cm^{-1}, measured in cyclohexane; cf. $[Fe(CO)_4\{P(OMe)_3\}]$: ν(C–O) 2062, 1991, 1961 and 1950 cm^{-1}, measured in cetane [9]). This formulation was confirmed through the isolation and full characterisation of crystalline $[Fe_2(CO)_8\{\mu\text{-}(MeO)_2PCH_2P(OMe)_2\}]$ and $[Fe_2(CO)_8\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}]$. The remainder of the octacarbonyls were isolated as oils and no attempt was made to characterise them.

Irradiation of light petroleum (b.p. 60–80 °C) solutions of these octacarbonyl derivatives with ultraviolet light was found to result in the evolution of carbon monoxide and subsequent column chromatographic purification of the reaction products led to the isolation of orange-red crystalline compounds characterised by means of elemental analysis as $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}R_2PYPR_2\}]$. The infrared spectra of these compounds exhibit very distinctive band patterns in the C–O stretching region (see Fig. 1a) which are very similar to those for $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}Ph_2PCH_2PPh_2\}]$ [5] and $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}(MeO)_2PN(Me)P(OMe)_2\}]$ [8].

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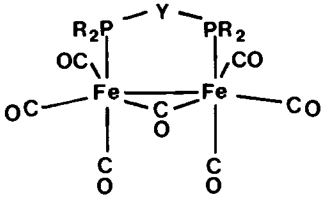
* See reference 7 for a preliminary communication of this investigation. Since the publication of our preliminary communication King et al. published the molecular structure of $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}(MeO)_2PN(Me)P(OMe)_2\}]$ [8].

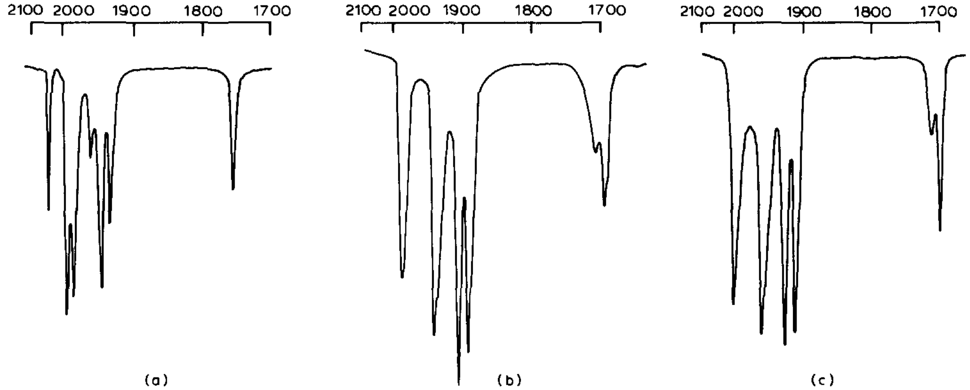
Furthermore the actual frequencies of the C–O stretching peaks are very similar to those for the corresponding pyrophosphite derivative (e.g. $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}]$: ν(C–O) 2054s, 1995s, 1988w, 1963s, 1947s, 1937m and 1755m cm^{-1}, measured in cyclohexane; cf. $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}(EtO)_2POP(OEt)_2\}]$: ν(C–O) 2063s 2010vs, 1975m, 1962s, 1950s, 1772m, and 1762m cm^{-1}, measured in cyclohexane [4]). This spectral evidence is interpreted in terms of structure I which is analogous to that established X-ray crystallographically for $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}Ph_2PCH_2PPh_2\}]$ [5] and $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}(MeO)_2PN(Me)P(OMe)_2\}]$ [8].



(I)

These compounds thus provide further examples of stable bis-substituted derivatives of $[Fe_2(CO)_9]$ but containing a single and not three bridging carbonyl groups as found for the parent nonacarbonyl [10].

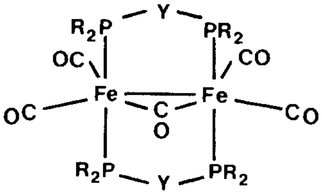
Treatment of light petroleum solutions of $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}R_2PYPR_2\}]$ with a slight excess of the appropriate ligand under photochemical conditions resulted in further substitution of carbonyl groups and the formation of new products characterised as $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}R_2PYPR_2\}_2]$. The infrared spectra of these compounds again reveal very distinctive band patterns in the C–O stretching region (Fig. 1b) comprising one bridging and four terminal carbonyl peaks of frequency very similar to those for $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(EtO)_2POP(OEt)_2\}_2]$ (e.g. $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$: ν(C–O) 1995s, 1947vs, 1913s, 1896s, and



(a) (b) (c)

Fig. 1. Cyclohexane solution infrared spectra, in the C–O stretching region, of (a) $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}]$, (b) $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$, and (c) $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$.

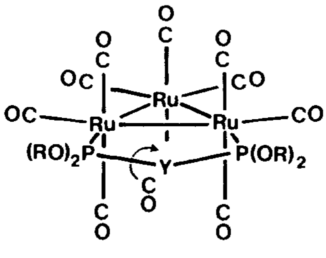
1697m cm^{-1}, measured in cyclohexane; cf. $[Fe_2(\mu\text{-CO})(CO)_4\{\mu\text{-(EtO)}_2POP(OEt)_2\}_2]$: ν(C–O) 2010s, 1955vs, 1929s, 1910s, 1720sh, 1710s, and 1700sh cm^{-1}, measured in cyclohexane). On the basis of this spectroscopic data it is proposed that these pentacarbonyl derivatives have structure II which is analogous to that established X-ray crystallographically for $[Fe_2(\mu\text{-CO})(CO)_4\{\mu\text{-(EtO)}_2POP(OEt)_2\}_2]$ [4] and $[Fe_2(\mu\text{-CO})(CO)_4\{\mu\text{-}F_2PN(Me)PF_2\}_2]$ [6].



(II)

The thermal reactions of either $[Fe_2(CO)_9]$ or $[Fe_2(\mu\text{-CO})(CO)_6\{\mu\text{-}R_2PYPR_2\}]$ with R_2PYPR_2 were found to contrast with their corresponding photochemical reactions in that they afforded products characterised by elemental analysis as mononuclear $[Fe(CO)_3\{R_2PYPR_2\}]$. The nuclearity of these species has been confirmed by means of an X-ray crystal structure determination on $[Fe(CO)_3\{(PhO)_2PN(Et)P(OPh)_2\}]$ [11]. Significantly irradiation of these mononuclear species with ultraviolet light did not lead to their decarbonylation and rearrangement of dinuclear $[Fe_2(\mu\text{-CO})(CO)_4\{\mu\text{-}R_2PYPR_2\}_2]$.

Cotton and Hanson have previously established that reaction of $[Ru_3(CO)_{12}]$ with $Ph_2PCH_2PPh_2$ in THF at ca. 50 °C affords the decacarbonyl derivative $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PCH_2PPh_2\}]$ [12]. It is thus not surprising that treatment of triruthenium dodecacarbonyl with an equimolar amount of $(RO)_2PYP(OR)_2$ (Y = N(Et), R = Ph or Me; Y = N(Me), R = Pr^i or Et) under either thermal or photochemical conditions leads to the formation of the bis-substituted derivatives $[Ru_3(CO)_{10}\{\mu\text{-(RO)}_2PYP(OR)_2\}]$. These compounds which were characterised by means of elemental analysis and infrared and NMR spectroscopy are assumed to contain the diphosphazane ligand coordinated in the bridging mode at equatorial positions, structure III, as found X-ray crystallographically for $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PN(Et)PPh_2\}]$ [13]. Significantly it was established that cleavage of the Ru–Ru bonds in $[Ru_3(CO)_{10}\{\mu\text{-(RO)}_2PYP(OR)_2\}]$ could be effected by irradiation with ultraviolet light in the presence of excess ligand. The products which were isolated



(III)

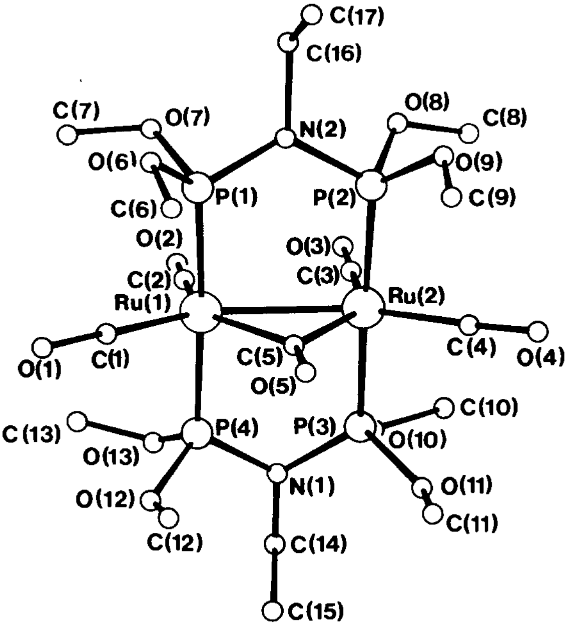


Fig. 2. The molecular stereochemistry of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$.

from solution were characterised by elemental analysis as dinuclear $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(RO)_2PYP(OR)_2\}_2]$. These are the first known derivatives of $[Ru_2(CO)_9]$ *. As anticipated the band patterns of the C–O stretching peaks in the infrared spectra of these pentacarbonyl compounds are very similar to those of their iron analogues (Fig. 1c) indicating that their structures are analogous. This was confirmed by means of an X-ray structure determination on $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ described below. These compounds are unstable in solution, particularly in polar solvents, and decompose slowly in non-polar solvents to $[Ru(CO)_3\{(RO)_2PYP(OR)_2\}]$, as identified by means of infrared spectroscopy.

Molecular structure of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$

The molecular stereochemistry of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ is illustrated in Fig. 2. The two ruthenium atoms, which are separated by a distance of 2.801(2) Å, corresponding to a formal ruthenium–ruthenium bond, are bridged not only by the two diphosphazane ligands but by a carbonyl group as well. Two of the terminal carbonyl groups are essentially orthogonal to the ruthenium–ruthenium vector (Ru(1)–Ru(2)–C(3) 94.0(5)°; Ru(2)–Ru(1)–C(2) 93.8(5)°) while the other two are almost collinear with it (Ru(1)–Ru(2)–C(4) 153.8(6)°; Ru(2)–Ru(1)–C(1) 153.9(5)°). All five carbonyl groups, as well as the ruthenium atoms, are essentially coplanar with the ruthenium–phosphorus vectors being essentially orthogonal to this plane. Bond lengths and angles are given in Tables 6 and 7 respectively; these show no unusual features.

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* Under appropriate reaction conditions $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}Ph_2PCH_2PPh_2\}_2]$ can also be synthesised (Unpublished results).

Experimental

All reactions were performed under an atmosphere of nitrogen in freshly redistilled solvents. The products are stable in air at room temperature in the crystalline state for at least 3 days. IR spectra (Table 1) were recorded in 0.5 mm NaCl cells on Perkin–Elmer 457 and 283 grating spectrometers. NMR spectra

TABLE 1

INFRARED SPECTROSCOPIC DATA (cm^{-1})

Y	R	ν(C–O)						
$[Fe_2(CO)_8\{\mu\text{-}R_2PYPR_2\}]$								
N(Et)	OPh	2066m	1994m	1959s,br	1950sh[a]			
N(Et)	OMe	2060m	1988m	1953s,br	1945sh[a]			
N(Me)	OPr^i	2058m	1982m	1952s,br	1938sh[a]			
N(Me)	OEt	2059m	1985m	1951s,br	1945sh[a]			
N(Et)	OCH_2	2053m	1997m	1982ms	1950vs,br[b]			
CH_2	OMe	2050m	1982m	1978sh	1945vs,br[a]			
CH_2	OPr^i	2043m	1978m	1938s	1930sh[a]			
CH_2	Ph	2040s	1995sh	1975s	1942s,br	1925sh[a]		
CH_2	Me	2037w	1973w	1930s,br[a]				
$[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}R_2PYPR_2\}]$								
N(Et)	OPh	2060s	2011s	2001s	1977m	1969s	1954m	1777m[a]
N(Et)	OMe	2054s	1995s	1988w	1963s	1947s	1937m	1755m[a]
N(Me)	OPr^i	2054s	1999s	1990m	1960s	1948s	1930s	1775m[a]
N(Me)	OEt	2054s	2002s	1994m	1967s	1950s	1938m	1760m[a]
N(Et)	OCH_2	2056s	2001vs	1987s	1955vs	1944sh	1765sh	1757m[b]
CH_2	OMe	2050m	1998s	1985m	1955sh	1948s	1775sh	1760m[a]
CH_2	OPr^i	2043m	1988s	1978m	1955m	1945s		1770m,br[a]
CH_2	Ph	2045m	1998m	1987s	1960ms	1949s	1932m	1768m[a]
CH_2	Me	2040s	1979s	1964s	1928s,br	1917sh		1735m,br[a]
$[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}R_2PYPR_2\}_2]$								
NEt	OPh	2010s	1963s	1939s	1912s	1727ms[a]		
NEt	OMe	1995s	1947s	1913s	1896s	1712sh	1697ms[a]	
NMe	OPr^i	1985ms	1925s	1901ms	1877s	1718m[a]		
NMe	OEt	1992s	1943s	1907s	1892s	1695ms[a]		
NEt	OCH_2	1996m	1955s	1925s	1910ms	1724m[b]		
CH_2	OMe	1965m	1914s	1890s	1870sh	1712sh	1703m[b]	
CH_2	OPr^i	1953m	1900s	1879s	1855m	1711m,br[a]		
CH_2	Ph	1948m	1898s	1870s	1850sh	1690m[b]		
CH_2	Me	1935ms	1885s	1857s	1835sh	1657m,br[b]		
$[Fe(CO)_3\{R_2PYPR_2\}]$								
NEt	OPh	2022ms	1958ms	1944s[a]				
NEt	OMe	1997s	1928s	1915s[a]				
$[Ru_3(CO)_{10}\{\mu\text{-}R_2PYPR_2\}]$								
NEt	OPh	2092m	2028s	2010s	1988m	1978m[a]		
NEt	OMe	2085m	2015s	2001s	1960m	1930m[a]		
NMe	OEt	2080m	2010s	2000s	1970ms	1935m[a]		
$[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}R_2PYPR_2\}_2]$								
NEt	OPh	2021s	1987ms	1948m	1932ms	1720m,br[a]		
NEt	OMe	1999s	1960s	1929s	1913s	1703ms[a]		
NMe	OPr^i	1990s	1942s	1920ms	1895s	1730m[a]		
NMe	OEt	1998ms	1965s	1925s	1910s	1700m[a]		

[a] Measured in cyclohexane. [b] Measured in CH_2Cl_2.

(Table 2) were recorded on Varian T60 and FT 80A spectrometers. Microanalyses (Table 3) were performed by the Microanalytical Section of the Department of Chemistry, University of Natal, Pietermaritzburg.

(1) $[Fe_2(CO)_8\{\mu\text{-}R_2PYPR_2\}]$. A toluene solution (40 cm^3) of R_2PYPR_2 (2 mmol) [14] was added dropwise to a stirred suspension of $[Fe_2(CO)_9]$ (1.45 g; 4 mmol) in toluene (100 cm^3) at room temperature and the reaction mixture stirred for 15 h. The resultant orange solution was filtered and the solvent removed under reduced pressure to afford a yellow brown oil. Purification of the product was, in general, not possible, but $[Fe_2(CO)_8\{\mu\text{-}(MeO)_2PCH_2P(OMe)_2\}]$ and $[Fe_2(CO)_8\{\mu\text{-}(CH_2O)_2PN(Et)P(OCH_2)_2\}]$ could be isolated as yellow crystalline products and recrystallised from petroleum ether (b.p. 60–80 °C). Yields: ca. 75–80%.

(Continued on p. 108)

TABLE 2

NMR SPECTROSCOPIC DATA

Y	R	$\delta(^1H)$ (ppm)			$\delta(^{31}P)$ [c] (ppm)
$[Fe_2(CO)_8\{R_2PYPR_2\}]$					
NEt	OCH_2	1.29t(3H)	3.69m(2H)	4.39m(8H) [a]	
CH_2	OMe	3.36t(2H)	3.85m(12H) [a]		
$[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}R_2PYPR_2\}]$					
NEt	OPh	1.43t(3H)	3.76m(2H)	7.36m(20H) [a]	
NEt	OMe	1.23t(3H)	3.35m(2H)	3.81t(12H) [a]	176.5
NMe	OPr^i	1.40t(3H)	2.57d(24H)	4.70q(4H) [a]	
NMe	OEt	1.30t(3H)	2.55t(12H)	4.00m(8H) [a]	
NEt	OCH_2	1.17t(3H)	3.06m(2H)	4.35t(8H) [a]	
CH_2	OMe	3.12t(2H)	3.81t(12H) [a]		203.4
CH_2	OPr^i	1.40d(24H)	3.00t(2H)	4.82m(4H) [a]	
CH_2	Me	1.75t(12H)	2.53t(2H) [a]		
CH_2	Ph	not sufficiently stable			
$[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}R_2PYPR_2\}_2]$					
NEt	OPh	1.33t(6H)	3.74m(4H)	7.25m(40H) [b]	176.3
NEt	OMe	1.17t(6H)	3.20m(4H)	3.70t(24H) [a]	
NMe	OPr^i	1.36d(48H)	2.65m(6H)	4.81m(8H) [a]	
NMe	OEt	1.30t(6H)	2.58t(24H)	4.05m(16H) [a]	
NEt	OCH_2	1.12t(6H)	3.01m(4H)	4.25t(16H) [a]	
CH_2	OMe	not sufficiently stable			
CH_2	OPr^i	not sufficiently stable			
CH_2	Ph	not sufficiently stable			
CH_2	Me	not sufficiently stable			
$[Fe(CO)_3\{R_2PYPR_2\}]$					
NEt	OPh	1.41t(3H)	3.56m(2H)	7.23s(20H) [a]	
NEt	OMe	not sufficiently stable			
$[Ru_3(CO)_{10}\{\mu\text{-}R_2PYPR_2\}]$					
NEt	OPh	1.43t(3H)	3.68m(2H)	7.25s(20H) [a]	
NEt	OMe	not measured			
NMe	OEt	not measured			
$[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}R_2PYPR_2\}_2]$					
NEt	OPh	not sufficiently stable			
NEt	OMe	1.22t(6H)	3.17m(4H)	3.65(24H) [a]	
NMe	OPr^i	1.34d(48H)	2.63t(6H)	4.78m(8H) [a]	
NMe	OEt	1.19t(24H)	2.63t(6H)	4.10m(16H) [a]	152

[a] Measured in acetone-d_6. δ scale (ppm) relative to TMS = 0. [b] Measured in $CDCl_3$. [c] Measured in acetone-d_6. δ scale (ppm) relative to H_3PO_4 = 0.

TABLE 3

MICROANALYTICAL DATA

Compound	Y	R	Analysis (Found(calcd.)(%))		
			C	H	N
$[\mathrm{Fe_2(CO)_8}\{\mu\text{-}\mathrm{R_2PYPR_2}\}]$					
	NEt	OCH$_2$	29.94	2.32	2.50
			(30.19)	(2.67)	(2.53)
	CH$_2$	OMe	28.35	2.76	
			(28.20)	(2.67)	
$[\mathrm{Fe_2}(\mu\text{-}\mathrm{CO})(\mathrm{CO})_6\{\mu\text{-}\mathrm{R_2PYPR_2}\}]$					
	NEt	OPh	50.55	3.34	1.92
			(50.48)	(3.21)	(1.78)
	NEt	OMe	29.23	3.11	2.64
			(29.05)	(3.17)	(2.61)
	NMe	OPr^i	37.65	5.01	2.23
			(37.80)	(4.88)	(2.20)
	NMe	OEt	33.20	3.86	2.38
			(33.16)	(3.97)	(2.42)
	NEt	OCH$_2$	29.11	2.76	3.02
			(29.27)	(2.44)	(2.63)
	CH$_2$	OMe	29.21	2.86	
			(29.26)	(2.62)	
	CH$_2$	OPr^i	38.60	4.81	
			(38.71)	(4.89)	
	CH$_2$	Me	32.41	3.07	
			(32.43)	(3.15)	
$[\mathrm{Fe_2}(\mu\text{-}\mathrm{CO})(\mathrm{CO})_4\{\mu\text{-}\mathrm{R_2PYPR_2}\}_2]$					
	NEt	OPh	56.73	4.18	2.30
			(56.74)	(4.20)	(2.32)
	NEt	OMe	28.93	4.80	3.90
			(28.65)	(4.78)	(3.93)
	NMe	OPr^i	40.73	6.81	3.08
			(41.06)	(6.84)	(3.09)
	NMe	OEt	35.15	5.84	3.38
			(34.76)	(5.79)	(3.53)
	NEt	OCH$_2$	28.97	3.66	3.91
			(29.08)	(3.70)	(3.99)
	CH$_2$	OMe	27.56	4.48	
			(27.61)	(4.29)	
	CH$_2$	OPr^i	42.17	6.90	
			(42.47)	(6.85)	
	CH$_2$	Me	33.99	5.38	
			(34.35)	(5.34)	
	CH$_2$	Ph	cannot obtain sufficiently pure		
$[\mathrm{Fe(CO)_3}\{\mathrm{R_2PYPR_2}\}]$					
	NEt	OPh	56.57	4.01	2.38
			(56.40)	(4.05)	(2.27)
	NEt	OMe	29.01	4.37	3.73
			(29.27)	(4.61)	(3.79)
$[\mathrm{Ru_3(CO)_{10}}\{\mu\text{-}\mathrm{R_2PYPR_2}\}]$					
	NEt	OPh	40.97	2.45	
			(40.76)	(2.37)	
	NEt	OMe	23.62	2.18	1.68
			(23.65)	(2.09)	(1.72)
	NMe	OEt	not determined		

TABLE 3 (continued)

Compound	Y	R	Analysis (Found(calcd.)(%))		
			C	H	N
$[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}R_2PYPR_2\}_2]$	NEt	OPh	52.83	3.86	2.16
			(52.77)	(3.86)	(2.17)
	NEt	OMe	25.54	4.32	3.48
			(25.44)	(4.24)	(3.49)
	NMe	OPr^i	37.21	6.13	2.79
			(37.35)	(6.22)	(2.81)
	NMe	OEt	31.32	5.16	3.21
			(31.22)	(5.20)	(3.17)

TABLE 4

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND ISOTROPIC THERMAL PARAMETERS ($Å^2 \times 10^3$) FOR $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$

	x	*y*	*z*	*U*
Ru(1)	2439(1)	1205(1)	340(1)	
Ru(2)	2593(1)	2681(1)	9676(1)	
P(1)	2348(3)	1556(2)	2124(3)	
P(2)	2531(3)	3088(2)	1435(3)	
P(3)	2641(3)	2329(2)	7880(3)	
P(4)	2545(3)	795(2)	8581(3)	
O(1)	3218(9)	−265(8)	1054(11)	89(4)
O(2)	270(10)	1207(8)	121(11)	94(4)
O(3)	450(10)	2896(7)	9575(11)	89(4)
O(4)	3674(10)	4073(8)	9118(11)	99(4)
O(5)	4452(8)	1854(6)	187(8)	61(3)
O(6)	3087(7)	1182(5)	2997(8)	50(3)
O(7)	1388(7)	1342(6)	2746(8)	56(3)
O(8)	1643(8)	3600(6)	1754(9)	65(3)
O(9)	3351(8)	3640(7)	1868(9)	71(3)
O(10)	1741(7)	2565(6)	7107(8)	59(3)
O(11)	3474(8)	2662(6)	7157(8)	58(3)
O(12)	3327(8)	181(6)	8318(9)	66(3)
O(13)	1639(8)	354(6)	8093(9)	67(3)
N(1)	2667(9)	1423(7)	7608(10)	49(3)
N(2)	2438(9)	2447(7)	2429(10)	52(3)
C(1)	2919(11)	311(9)	787(13)	53(4)
C(2)	1097(12)	1196(9)	215(13)	54(4)
C(3)	1266(12)	2823(9)	9570(13)	53(4)
C(4)	3266(13)	3523(11)	9309(15)	71(5)
C(5)	3596(10)	1844(8)	100(11)	42(4)
C(6)	4087(11)	1208(9)	2761(13)	57(6)
C(7)	1139(13)	580(11)	2965(15)	75(6)
C(8)	1484(14)	4294(11)	1171(16)	83(6)
C(9)	4341(14)	3452(11)	1777(16)	85(6)
C(10)	1538(13)	3338(11)	6947(15)	76(6)
C(11)	4431(14)	2584(11)	7422(15)	77(6)
C(12)	4312(14)	302(11)	8650(16)	81(6)
C(13)	1306(13)	−311(11)	8661(15)	75(5)
C(14)	2686(16)	1175(11)	6394(16)	82(6)
C(15)	3428(27)	934(22)	5974(30)	100
C(15′)[a]	1958(42)	1035(32)	5856(46)	100
C(16)	2365(16)	2723(11)	3608(16)	73(6)
C(17)	3117(28)	2882(22)	4178(31)	100
C(17′)[a]	1714(42)	2797(31)	4053(46)	100

[a] C(15) and C(17) are disordered between two alternate positions.

(2) $[Fe_2(\mu\text{-}CO)(CO)_6\{\mu\text{-}R_2PYPR_2\}]$. A light petroleum ether (b.p. 60–80 °C) solution (150 cm^3) of $[Fe_2(CO)_8\{\mu\text{-}R_2PYPR_2\}]$ was irradiated with UV light for 4 h. The solvent was removed under reduced pressure and the residue chromatographed on an alumina column. Elution with 1/2 benzene/petroleum ether (b.p. 60–80 °C) afforded a red band which was collected. The solvent was removed under reduced pressure to afford a red crystalline compound which was recrystallised from petroleum ether (b.p. 60–80 °C). Yields: ca. 65–75%.

(3) $[Fe_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}R_2PYPR_2\}_2]$. A light petroleum ether (b.p. 60–80 °C) solution (150 cm^3) of $[Fe_2(CO)_8\{\mu\text{-}R_2PYPR_2\}]$ (2 mmol) and R_2PYPR_2 (2.1 mmol) was irradiated with UV light for 15 h. The solvent was removed under reduced pressure and the residue, in general, chromatographed on an alumina

TABLE 5

ANISOTROPIC THERMAL FACTORS ($Å^2 \times 10^3$) FOR $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	42(1)	29(1)	37(1)	2(1)	1(1)	−1(1)
Ru(2)	50(1)	30(1)	39(1)	2(1)	3(1)	−2(1)
P(1)	51(3)	38(3)	39(2)	3(2)	6(2)	1(2)
P(2)	75(3)	35(3)	42(3)	−1(2)	0(2)	1(2)
P(3)	52(3)	40(3)	40(3)	7(2)	2(2)	−2(2)
P(4)	55(3)	35(3)	41(3)	−3(2)	0(2)	−1(2)

The temperature factor exponent takes the form $-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2Uhka^*b^*)$

TABLE 6

BOND LENGTHS (Å) FOR $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$

Ru(1)–Ru(2)	2.801(2)	Ru(1)–P(1)	2.291(4)
Ru(1)–P(4)	2.295(4)	Ru(1)–C(1)	1.83(2)
Ru(1)–C(2)	1.89(2)	Ru(1)–C(5)	2.06(2)
Ru(2)–P(2)	2.290(4)	Ru(2)–P(3)	2.302(4)
Ru(2)–C(3)	1.89(2)	Ru(2)–C(4)	1.85(2)
Ru(2)–C(5)	2.08(2)	P(1)–O(6)	1.63(1)
P(1)–O(7)	1.61(1)	P(2)–O(8)	1.61(1)
P(2)–O(9)	1.61(1)	P(3)–O(10)	1.63(1)
P(3)–O(11)	1.60(1)	P(4)–O(12)	1.60(1)
P(4)–O(13)	1.61(1)	P(1)–N(2)	1.66(1)
P(2)–N(2)	1.69(1)	P(3)–N(1)	1.67(1)
P(4)–N(1)	1.66(1)	C(1)–O(1)	1.17(2)
C(3)–O(3)	1.16(2)	C(4)–O(4)	1.17(2)
C(5)–O(5)	1.21(2)	O(6)–C(6)	1.44(2)
O(7)–C(7)	1.45(2)	O(8)–C(8)	1.46(2)
O(9)–C(9)	1.44(2)	O(10)–C(10)	1.44(2)
O(11)–C(11)	1.39(2)	O(12)–C(12)	1.45(2)
O(13)–C(13)	1.47(2)	N(1)–C(14)	1.56(2)
N(2)–C(16)	1.54(2)	C(14)–C(15)	1.25(4)
C(14)–C(15′)	1.24(6)	C(16)–C(17)	1.29(4)
C(16)–C(17′)	1.08(5)		

column. Elution with 1/2 dichloromethane/petroleum ether (b.p. 60–80 °C) afforded an orange band from which a red/orange crystalline compound could be obtained. Recrystallisation was effected from benzene/petroleum ether (b.p. 60–80 °C).

The following compounds were not chromatographed owing to their decomposition on the column: Y = N(Et), R = CH_2O; the product was crystallised from H_2O. Y = CH_2, R = Ph; the solid which separated from the reaction mixture was repeatedly washed with cyclohexane. Y = CH_2, R = Me, OMe and OPr^i; these products were crystallised from n-hexane. Yields: ca. 50–60%.

TABLE 7

BOND ANGLES (°) FOR $[Ru_2(\mu\text{-CO})(CO)_4\{\mu\text{-(MeO)}_2PN(Et)P(OMe)_2\}_2]$

P(1)–Ru(1)–Ru(2)	91.2(1)	P(4)–Ru(1)–Ru(2)	91.5(1)
C(1)–Ru(1)–Ru(2)	153.9(5)	C(2)–Ru(1)–Ru(2)	93.8(5)
P(1)–Ru(1)–P(4)	177.1(2)	C(1)–Ru(1)–P(1)	89.0(5)
C(1)–Ru(1)–P(4)	88.2(5)	C(2)–Ru(1)–P(1)	90.5(5)
C(2)–Ru(1)–P(4)	90.1(5)	C(1)–Ru(1)–C(2)	112.2(7)
C(5)–Ru(1)–Ru(2)	47.7(4)	C(5)–Ru(1)–P(1)	91.7(4)
C(5)–Ru(1)–P(4)	89.6(4)	C(5)–Ru(1)–C(1)	106.3(6)
C(5)–Ru(1)–C(2)	141.5(6)	P(3)–Ru(2)–Ru(1)	91.2(1)
P(2)–Ru(2)–Ru(1)	91.5(1)	P(2)–Ru(2)–P(3)	177.2(2)
C(4)–Ru(2)–Ru(1)	153.8(6)	C(4)–Ru(2)–P(3)	88.3(6)
C(4)–Ru(2)–P(2)	89.6(6)	C(3)–Ru(2)–Ru(1)	94.0(5)
C(3)–Ru(2)–P(3)	90.9(5)	C(3)–Ru(2)–P(2)	88.2(5)
C(3)–Ru(2)–C(4)	112.3(8)	C(5)–Ru(2)–Ru(1)	47.2(4)
C(5)–Ru(2)–P(3)	91.1(4)	C(5)–Ru(2)–P(2)	91.3(4)
C(5)–Ru(2)–C(4)	106.6(7)	C(5)–Ru(2)–C(3)	141.2(6)
O(6)–P(1)–Ru(1)	118.1(4)	O(7)–P(1)–Ru(1)	116.8(4)
O(7)–P(1)–O(6)	96.7(5)	N(2)–P(1)–Ru(1)	118.7(5)
N(2)–P(1)–O(6)	102.0(6)	N(2)–P(1)–O(7)	100.8(6)
N(2)–P(2)–Ru(2)	117.9(5)	O(9)–P(2)–Ru(2)	118.3(5)
O(9)–P(2)–N(2)	104.5(6)	O(8)–P(2)–Ru(2)	117.2(5)
O(8)–P(2)–N(2)	98.5(6)	O(8)–P(2)–O(9)	96.7(6)
O(10)–P(3)–Ru(2)	117.0(4)	O(11)–P(3)–Ru(2)	117.6(4)
O(10)–P(3)–O(11)	98.3(6)	N(1)–P(3)–Ru(2)	117.7(5)
N(1)–P(3)–O(10)	99.1(6)	N(1)–P(3)–O(11)	103.8(6)
O(12)–P(4)–Ru(1)	118.1(4)	O(13)–P(4)–Ru(1)	116.6(5)
O(13)–P(4)–O(12)	97.1(6)	N(1)–P(4)–Ru(1)	117.9(5)
N(1)–P(4)–O(12)	104.4(6)	N(1)–P(4)–O(13)	99.2(6)
P(4)–N(1)–P(3)	121.5(8)	C(14)–N(1)–P(3)	118(1)
C(14)–N(1)–P(4)	119(1)	C(16)–N(2)–P(1)	121(1)
C(16)–N(2)–P(2)	117(1)	P(1)–N(2)–P(2)	120(1)
O(1)–C(1)–Ru(1)	178(2)	O(2)–C(2)–Ru(1)	178(2)
O(3)–C(3)–Ru(2)	175(2)	O(4)–C(4)–Ru(2)	177(2)
O(5)–C(5)–Ru(1)	138(1)	O(5)–C(5)–Ru(2)	136(1)
Ru(1)–C(5)–Ru(2)	85.1(5)	C(6)–O(6)–P(1)	118(1)
C(7)–O(7)–P(1)	122(1)	C(8)–O(8)–P(2)	119(1)
C(9)–O(9)–P(2)	121(1)	C(10)–O(10)–P(3)	119(1)
C(11)–O(11)–P(3)	123(1)	C(12)–O(12)–P(4)	119(1)
C(13)–O(13)–P(4)	119(1)	C(15)–C(14)–N(1)	121(3)
C(15′)–C(14)–N(1)	123(3)	C(17)–C(16)–N(2)	121(2)
C(17′)–C(16)–N(2)	126(4)	C(15)–C(14)–C(15′)	113(4)
C(17)–C(16)–C(17′)	113(4)		

(4) $[Ru_3(CO)_{10}\{\mu\text{-}R_2PYPR_2\}]$. A cyclohexane solution (150 cm^3) of $[Ru_3(CO)_{12}]$ (1 mmol) and R_2PYPR_2 (1.1 mmol) was irradiated with UV light for 2 h. The solution was reduced by evaporation at low pressure to approximately one tenth of its volume and allowed to stand for 15 h. The red crystalline compound which separated was recrystallised from petroleum ether (b.p. 60–80 °C) Yields: ca. 80–85%.

(5) $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}R_2PYPR_2\}_2]$. A cyclohexane solution (150 cm^3) of $[Ru_3(CO)_{12}]$ (1 mmol) and R_2PYPR_2 (3 mmol) was irradiated with UV light for 1 h. The solvent was removed under reduced pressure, the residue dissolved in diethyl ether and the solution allowed to stand at −10 °C for 48 h. The yellow crystalline compound which separated was recrystallised from diethyl ether. Yields: ca. 60–70%.

X-ray crystallography of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$

Crystal data: $C_{17}H_{34}O_{13}N_2P_4Ru_2$; monoclinic, a 14.060(5), b 18.088(7), c 12.305(4) Å, β 90.96(2)°; V 3128.9Å^3; D_c 1.70 g cm^{-3}, $Z = 4$; space group $P2_1/n$ from systematic absences; μ(Mo-K_α) 21.05 cm^{-1}. Yellow needles of $[Ru_2(\mu\text{-}CO)(CO)_4\{\mu\text{-}(MeO)_2PN(Et)P(OMe)_2\}_2]$ were grown from a diethyl ether solution. A crystal of dimensions 0.80 × 0.15 × 0.40 mm was placed on a Philips PW 1100 four-circle diffractometer and the cell parameters determined from accurate measurements of the positions of 20 strong reflections in the angular range $15 \leq 2\theta \leq 25°$ using graphite monochromated Mo-K_α radiation (λ 0.71069 Å). Diffraction intensities were measured in the range $2 \leq 2\theta \leq 40°$ using the ω–2θ scan technique. Three standard reflections, measured after every 50 reflections, showed no decrease in intensity during data collection. Lorentz and polarisation corrections, but no absorption corrections, were applied and equivalent reflections average to give 2384 unique observed ($I > 3\sigma(I)$) intensities which were used to solve and refine the structure.

Structure determination and refinement. The positions of the two Ru atoms were located using the Patterson method, the remaining non-hydrogen atoms being readily locatable in a subsequent electron-density map phased on the Ru atoms. The structure was refined by full-matrix least-squares methods with the Ru and P atoms assigned anisotropic temperature factors and the remaining atoms all assigned individual isotropic temperature factors. The methyl carbon atoms of both NEt groups are disordered between two alternate positions. Refinement of their site occupation factors (with a fixed isotropic thermal factor $U = 0.100$ Å^2) indicates a roughly equal occupation of these two positions for both carbon atoms viz. C(15) and C(17). The H atoms were not located. The refinement converged at a final conventional R factor of 0.058. Final atomic coordinates and associated thermal parameters are given in Tables 4 and 5.

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