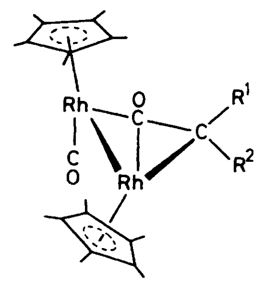
Electrophilic Behaviour of Dicarbonylbis(pentamethylcyclopentadienyl)-dirhodium towards Diazoalkanes and Low-valent Platinum Compounds: *X*-Ray Crystal Structure of $[PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$ †

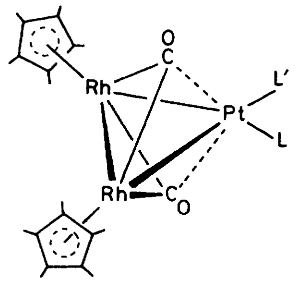
By **Michael Green, Rona M. Mills, Geoffrey N. Pain, F. Gordon A. Stone,** and **Peter Woodward,**
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The diazoalkanes $R^1R^2CN_2$ react with the dirhodium compound $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ to give the complexes $[Rh_2(\mu\text{-}CR^1R^2)(CO)_2(\eta\text{-}C_5Me_5)_2]$ ($R^1 = R^2 = H$ or CF_3; $R^1 = H$, $R^2 = CO_2Et$; $R^1 = H$, $R^2 = CH{=}CH_2$), the i.r. and n.m.r. data for which are reported and discussed. The dirhodiumplatinum compounds $[PtRh_2(\mu\text{-}CO)_2(cod)(\eta\text{-}C_5Me_5)_2]$ (cod = cyclo-octa-1,5-diene), $[PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$, and $[PtRh_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5Me_5)_2]$ have been isolated from reactions between low-valent platinum species and $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ or $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$. Spectroscopic properties are reported which are in accord with molecular structures in whch PtL_2 fragments are ' complexed ' with a $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ molecule giving rise to a $PtRh_2$ triangle semi-triply bridged by two CO ligands. This has been confirmed by an *X*-ray diffraction study on $[PtRh_2(\mu_3\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$, crystals of which are triclinic, space group $P\bar{1}$, in a unit cell with $a = 11.185(3)$, $b = 13.278(7)$, $c = 15.443(9)$ Å, $\alpha = 102.98(5)$, $\beta = 92.18(4)$, $\gamma = 105.88(4)°$, and $Z = 2$. The structure was solved to R 0.056 (R' 0.058) from 4 285 observable independent reflections [$I \geqslant 3.0\sigma(I)$] collected at 220 K in the range $2\theta \leqslant 50°$. The molecule is based on a triangle of metal atoms [Rh–Rh 2.647(2), Pt–Rh 2.618(2) and 2.691(2) Å]. The platinum atom is in a planar environment with respect to the two rhodium atoms and the CO and the PPh_3 ligands to which it is terminally bound. The longer Pt–Rh bond is essentially *trans* to CO. On either face of the metal triangle two other CO ligands bridge the Rh–Rh bond and lean towards the platinum in a semi-triply bridging manner [Pt–μ-CO (mean) 2.52 Å]. Each rhodium is η^5-co-ordinated to a C_5Me_5 group, as expected. The reaction between $[Ni(cod)_2]$ and $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ affords the thermally unstable and air sensitive complex $[NiRh_2(\mu\text{-}CO)_2(cod)(\eta\text{-}C_5Me_5)_2]$, while the salt $[PtRh_2(\mu\text{-}CO)(\mu\text{-}NO)(cod)(\eta\text{-}C_5Me_5)_2][PF_6]$ has been prepared from $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][PF_6]$ and $[Pt(cod)_2]$. The i.r. and n.m.r. data for these species are discussed.

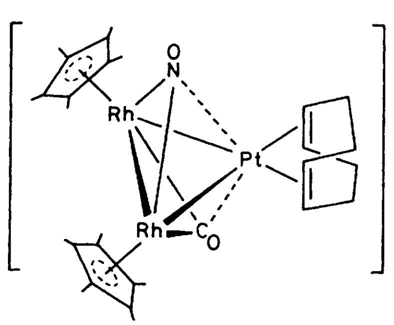
RECENTLY, Nutton and Maitlis [1] synthesised the compound $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$, a discovery of considerable importance, since by employing strategies based on isolobal relationships [2] it should be possible to use this compound as a precursor to many new metal complexes. A theoretical treatment [3] of the as yet unreported species $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ has revealed that it possesses a donor $3a_1$ and an acceptor $2b_2$ orbital which are similar in character to the filled π and vacant π^* orbitals of ethylene. This would equally apply to the pentamethylcyclopentadienyl analogue. Moreover, because of the isolobal relationship between the groups CH_2 and $Rh(CO)(\eta\text{-}C_5H_5)$ it follows [4] that the bonding in cyclopropane and in the dirhodium complex [5] $[Rh_2(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5H_5)_2]$ is entirely analogous. With this knowledge available we have investigated reactions of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ with diazoalkanes, and with zerovalent platinum complexes. Because of the isolobal relationship between the three species CH_2, PtL_2, and $Rh(CO)(\eta\text{-}C_5Me_5)$, it was anticipated that the products would be of the type $[Rh_2(\mu\text{-}CR_2)(CO)_2(\eta\text{-}C_5Me_5)_2]$ and $[Rh_2(\mu\text{-}PtL_2)(CO)_2(\eta\text{-}C_5Me_5)_2]$, respectively. Some of the results have been briefly communicated.[6,7] Concurrently with our studies involving diazoalkanes, two other research groups [8,9] independently discovered that CR_2 fragments could be added to $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ using these reagents; a process analogous to the cyclopropanation of ethylene. It should be noted that the



	R^1	R^2
(1)	H	H
(2)	CF_3	CF_3
(3)	H	CO_2Et
(4)	H	$CH{=}CH_2$



	L	L′
(5)	cod	
(6)	CO	PPh_3
(7)	PPh_3	C_2H_4
(9)	CO	CO



(11)

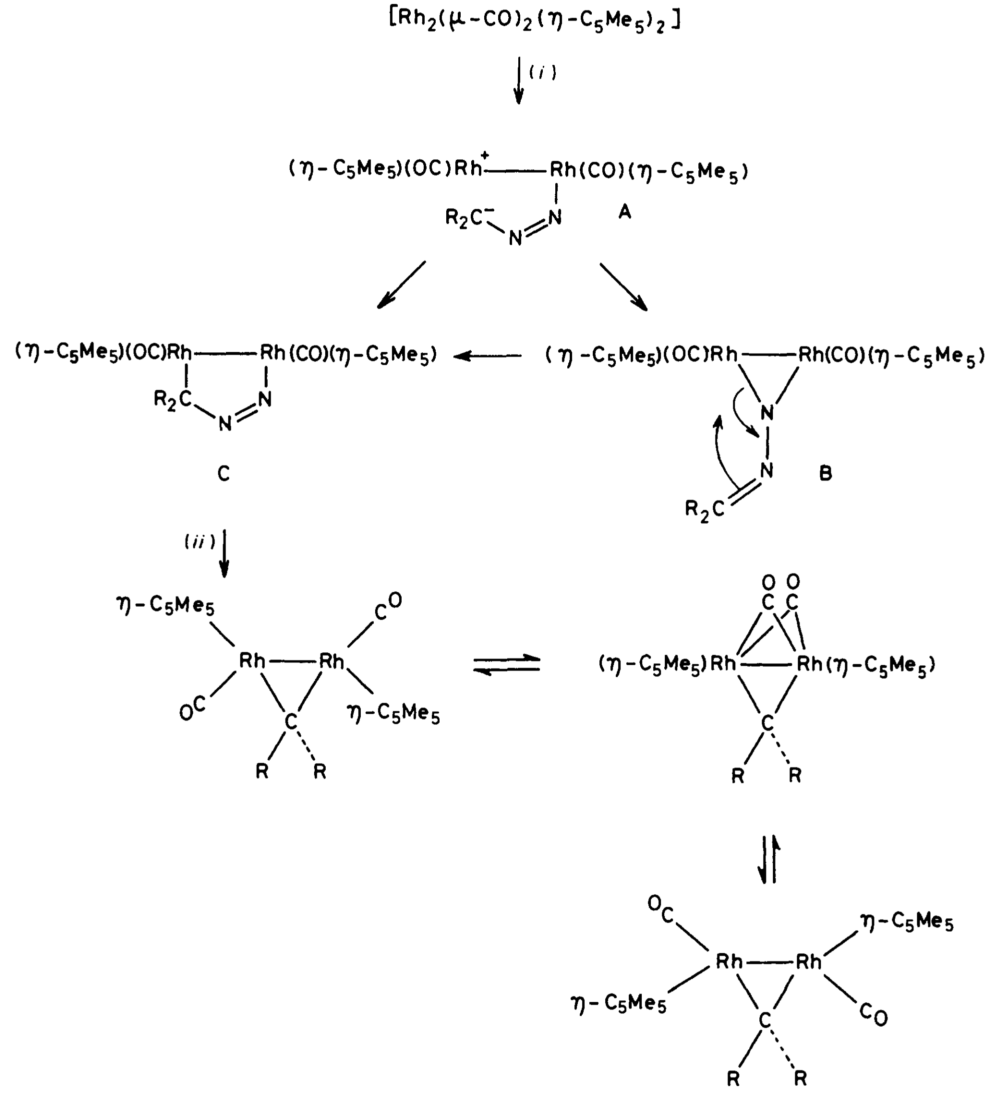
---

† Di-μ_3-carbonyl-1-carbonyl-2,3-bis(η-pentamethylcyclopentadienyl)-1-triphenylphosphine-*triangulo*-platinumdirhodium(2 *Pt–Rh*)(*Rh–Rh*).

compound $[Rh_2(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5H_5)_2]$, mentioned above, was prepared[5] by reacting the mononuclear rhodium compound $[Rh(CO)_2(\eta\text{-}C_5H_5)]$ with *N*-methyl-*N*-nitrosourea in boiling benzene. With the hindsight of more recent work in this area,[10] it seems likely that in this synthesis the product forms by addition of a carbene-like $Rh(CO)(\eta\text{-}C_5H_5)$ fragment to an intermediate $H_2C{=}Rh(CO)(\eta\text{-}C_5H_5)$.

RESULTS AND DISCUSSION

Reactions of Diazoalkanes.—The blue compound $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ reacts essentially quantitatively with diazoalkanes in diethyl ether at 0—20 °C to give red crystalline complexes (1)—(4), with no observable intermediates. A possible pathway for formation of the products is shown in Scheme 1. In view of the orbital similarities between $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ and C_2H_4, referred to above, a dipolar transition state A, analogous to those implicated in the (3 + 2) cycloaddition of diazoalkanes to alkenes,[11] seems reasonable. Collapse of A to give C, followed by loss of nitrogen, would afford the observed products. However, Curtis and co-workers[12] have isolated the complex $[Mo_2(\mu\text{-}N_2CPh_2)(CO)_4(\eta\text{-}C_5H_5)_2]$, from the reaction between $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and Ph_2CN_2 and shown that this molecule contains an *N*-bonded diazoalkane bridge, like B of Scheme 1. Moreover, on heating, the complex $[Mo_2(\mu\text{-}N_2CPh_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ releases nitrogen and affords $[Mo_2(\mu\text{-}CPh_2)(CO)_4(\eta\text{-}C_5H_5)_2]$. Hence in the synthesis of compounds (1)—(4) it is possible that a dirhodium species B is involved in the reaction pathway.



Scheme 1 (*i*) R_2CN_2, (*ii*) $- N_2$

The i.r. spectra of (1)—(4) in the carbonyl stretching region are as expected (Table 1), with (1) and (2) showing one strong band for the terminal CO asymmetric stretching vibration, and (3) and (4) exhibiting an additional weak band at higher frequency, assigned to the symmetric stretching vibration. Compound (1) has its CO stretch at lower frequency than $[Rh_2(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5H_5)_2]$ (1 984 cm^{-1}),[5] as expected, since η-C_5Me_5 is a better σ-donor than C_5H_5. This factor would also account for the resonance due to the μ-CH_2 group in the ^1H n.m.r. spectrum of (1) occurring (δ 5.92) upfield from the corresponding signal (δ 7.07)[5] in the η-C_5H_5 complex.

The ^{13}C n.m.r. spectra for (1) and (3), data for which are given in the Experimental section, show that the CO ligands undergo site exchange. This property is commonly observed with bridged dimetal complexes having CO or CNR ligands disposed *trans* about a metal–metal bond,[13] as is found[5] in $[Rh_2(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5H_5)_2]$ and more recently[8] in $[Rh_2\{\mu\text{-}C(CO_2Me)_2\}(CO)_2(\eta\text{-}C_5Me_5)_2]$. For compound (1), the room-temperature ^{13}C n.m.r. spectrum shows a triplet resonance [δ 196.5 p.p.m., J(RhC) 44 Hz] for the CO ligands. At −40 °C, however, the spectrum corresponds to the static structure, with the CO signal a doublet [δ 196.5 p.p.m., J(RhC) 88 Hz]. From the data, $\Delta G_{T_c}^{\ddagger}$ for the dynamic process is estimated to be 46 kJ mol^{-1}, which may be compared with values of 48 kJ mol^{-1} for pair-wise CO scrambling in the complex $[Rh_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)(CO)_2(\eta\text{-}C_5H_5)_2]$,[14] and 58 kJ mol^{-1} for CO/CNBu^t ligand site-exchange in $[Rh_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)(CO)(CNBu^t)(\eta\text{-}C_5H_5)_2]$.[15]

TABLE 1

Physical and analytical[a] data for the complexes $[Rh_2(\mu\text{-}CR^1R^2)(CO)_2(\eta\text{-}C_5Me_5)_2]$

	Compound[b]				Analysis (%)	
	R^1	R^2	M.p. (θ_c/°C)	ν(CO)[c]/cm^{-1}	C	H
(1)[d]	H	H	170	1 945s	51.7 (50.6)	6.2 (5.9)
(2)	CF_3	CF_3		1 972s	44.1 (44.0)	5.0 (4.4)
(3)	H	CO_2Et	146	1 981w, 1 959s	51.0 (50.5)	6.0 (5.9)
(4)	H	CH=CH_2	78	1 959w, 1 942s	53.0 (52.5)	6.3 (6.0)

[a] Calculated values are given in parentheses. [b] All complexes are red. [c] In hexane. [d] M (mass spectrum): Found 546, calc. 546.

In the ^{13}C n.m.r. spectra of (1) and (3) the resonances for the ligated μ-C atoms do not change their chemical shifts nor their J(RhC) values with temperature. This implies that the bridging μ-CH_2 and μ-C(H)CO_2Et groups do not participate in the dynamic process, an observation consistent with the view[16] that μ-CR_2 groups are both better σ-donors and π-acceptors than CO. The mechanism for dynamic behaviour is presumed to proceed (Scheme 1) *via* a triply-bridging intermediate. This intermediate could be attained by concerted rotation of the two Rh(CO)(η-C_5Me_5) moieties around each Rh–μ-C bond, with the CO ligands traversing the potential surface of electron density between the metal atoms. The fact that the CO groups of the unsymmetrically substituted alkylidene-bridge complex (3) retain their chemical identities while moving between rhodium atoms, as evidenced by the observation in the room-temperature spectrum of two triplet signals for these ligands, lends support to the proposed mechanism. Independent rotation of one Rh(CO)(η-C_5Me_5) fragment would also provide a pathway for equivalencing the CO groups, but would require passage through a *cis* isomer which for η-C_5Me_5 ligands would be sterically crowded. The process of forming the triply-bridged intermediate (Scheme 1) must involve lengthening of the Rh–CO and C–O bonds and decreasing the Rh–C–O angles from *ca.* 180 to 140°. In this context it is interesting to compare the CO ligand geometries of $[Rh_2(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5H_5)_2]$,[5] $[Rh_2\{\mu\text{-}C(CO_2Me)_2\}(CO)_2(\eta\text{-}C_5Me_5)_2]$, and $[Rh_2(\mu\text{-}C_5Br_4)(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$,[8] since the configurations adopted exemplify three stages in the dynamic process. The first compound has terminal and essentially linear CO ligands (Rh–C–O 177°), the second complex has semi-bridging groups (Rh–C–O 166°), while the last species has symmetrically bridging groups (Rh–C–O 140°).

The addition of diazoalkanes across certain metal–metal bonds has now become a widely employed method for preparing bridged alkylidene complexes. In addition to the work on the dirhodium species reported here, and elsewhere,[8,9] diazoalkanes have been shown to afford compounds with $\overline{M(\mu\text{-}CR_2)M}$ rings in reactions with $[Pt_2Cl_2(\mu\text{-}dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$),[17] $[Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)(\eta\text{-}C_5H_5)_2]$,[18] $[Mo_2(CO)_4(\eta\text{-}C_5H_4R)_2]$ (R = H or Me),[12] $[Co_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$,[19] $[Fe_2(\mu\text{-}NO)_2(\eta\text{-}C_5H_5)_2]$,[20] and $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(C_6H_{11})_3\}]$.[21] Several of these studies have been discussed in an important review.[22]

Reactions of Platinum(0) *Compounds.*—Ethylene complexes of platinum(0) are well known. Because of the previously discussed[3] similarity between the valence orbitals of ethylene and $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ it seemed likely that the pentamethylcyclopentadienyl species $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ would readily combine with PtL_2 fragments, isolobal with CH_2,[3,23] to give stable platinumdirhodium cluster species. While the application of the 18-electron rule implies metal–metal double bonds in the compounds $[M_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ (M = Co or Rh), theoretical treatments[3,24] lead to the conclusion that the two halves of these molecules are held together by highly delocalized bridge bonding *via* the carbonyls. Nevertheless, in these dimetal compounds there is an acceptor orbital available for bonding an incoming nucleophilic metal fragment. In a subsequent paper we report[25] the addition of an $Fe(CO)_4$ moiety, isolobal with PtL_2, to $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ affording a cluster compound $[FeRh_2(CO)_6(\eta\text{-}C_5Me_5)_2]$.

Addition of $[\mathrm{Pt(cod)_2}]$ (cod = cyclo-octa-1,5-diene) to $[\mathrm{Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2}]$ in dichloromethane at room temperature afforded in quantitative yield a yellow-brown crystalline compound (5), formulated as $[\mathrm{PtRh_2(\mu\text{-}CO)_2(cod)(\eta\text{-}C_5Me_5)_2}]$ on the basis of analysis, the mass spectrum, and i.r. and n.m.r. data. The i.r. spectrum showed a very low-frequency CO stretch (1 708 cm^{-1}) suggesting that the CO ligands are interacting with all three metal atoms. This is confirmed by the ^{13}C n.m.r. spectrum which shows a single CO resonance [δ 251.5 p.p.m.] appearing as a symmetrical triplet [*J*(RhC) 44 Hz] but with platinum satellites. The magnitude of the ^{195}Pt–^{13}C coupling (239 Hz) indicates a significant element of $\overline{\mathrm{Rh_2(\mu\text{-}CO)Pt}}$ bonding. In the cation $[\mathrm{MnPt(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)}]^+$, which has been shown by *X*-ray crystallography [26] to contain a semi-bridging CO ligand, *J*(PtC) is 81 Hz. Other resonances in the ^{13}C n.m.r. spectrum of (5), and also the ^{1}H spectrum, are consistent with the structure proposed. Compound (5) is isoelectronic (46 electrons) with the complex $[\mathrm{Fe_2Pt(CO)_8(cod)}]$.[27] The latter may be regarded as an adduct formed by the transient [28] $[\mathrm{Fe_2(CO)_8}]$ with Pt(cod), and in the context of isolobal relationships both compound (5) and the di-ironplatinum species are analogous to the alkeneplatinum complexes [Pt(alkene)(cod)].[29]

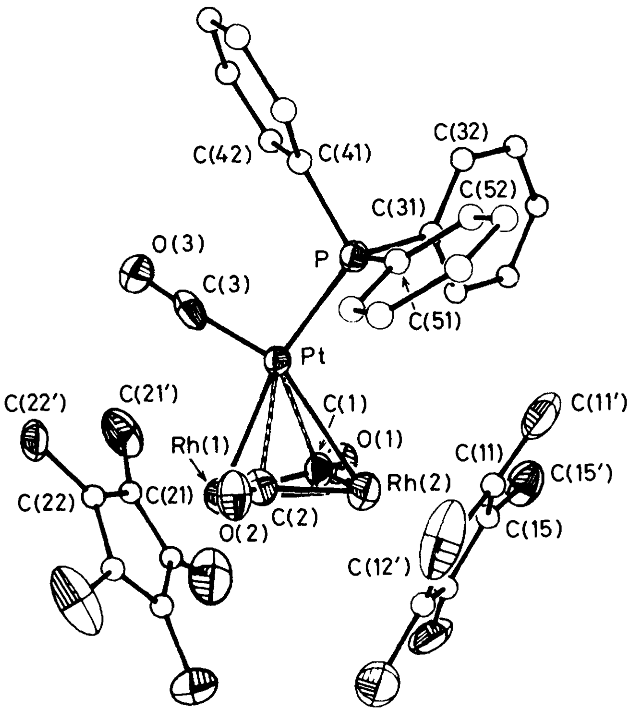


FIGURE 1 Molecular structure of the complex $[\mathrm{PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2}]$ (6)

Treatment of $[\mathrm{Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2}]$ with $[\mathrm{Pt(C_2H_4)(PPh_3)_2}]$ (1 : 1 mol ratio) afforded a complex mixture, including unreacted dirhodium compound and $[\mathrm{Pt(PPh_3)}_n]$ (n = 3—4). By chromatography the major product was isolated and formulated as $[\mathrm{PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2}]$ (6). The i.r. spectrum exhibited bands at 2 002 and 1 711 cm^{-1} corresponding to terminal and bridging CO ligands, respectively. The ^{1}H n.m.r. spectrum indicated two non-equivalent η-$\mathrm{C_5Me_5}$ groups, and this was confirmed by the ^{13}C spectrum which also showed resonances for terminal [δ 184.4 p.p.m., *J*(PtC) 1 810, *J*(RhC) 10, 4 Hz] and bridging [δ 252.7 p.p.m., *J*(PtC) 125, *J*(RhC) 44 Hz] carbonyl ligands. The ^{31}P n.m.r. spectrum revealed a doublet signal [δ 26.8 p.p.m., *J*(RhP) 15, *J*(PtP) 4 004 Hz] corresponding to a Pt-$(\mathrm{PPh_3})$ group with coupling of the phosphorus to one rhodium atom. The ^{195}Pt spectrum confirmed the *J*(PtP) coupling value and showed additional coupling to inequivalent ^{103}Rh nuclei.

Compound (6) undergoes reversible one-electron oxidation at 0.3 V in $\mathrm{CH_2Cl_2}$. A second irreversible oxidation occurs at *ca.* 0.8 V. Chemical oxidation to the radical cation was achieved quantitatively with $[\mathrm{Fe(\eta\text{-}C_5H_5)_2}][\mathrm{PF_6}]$ in $\mathrm{CH_2Cl_2}$ affording $[\mathrm{PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2}][\mathrm{PF_6}]$ [ν(CO) 2 047 and 1 791 cm^{-1}].

Although the n.m.r. data established the gross features of the molecular structure of (6), it was decided to undertake an *X*-ray crystallographic study because of the novelty of the compound, and to establish the details of the CO bridging. The molecular structure is shown in Figure 1, together with the atom-numbering scheme, and the results are summarised in Tables 2 and 3. The three metal atoms and the centroids of the $\mathrm{C_5Me_5}$ rings form a plane which almost coincides with the plane defined by Pt, C(3), O(3), and P (dihedral angle 3°). The $\mathrm{C_5Me_5}$ rings are perpendicular to the plane of the metal atoms and tilted away from the $\mathrm{Pt(CO)(PPh_3)}$ group, towards each other. The space-filling and stereo representations (Figure 2) show the crowded disposition of the staggered $\mathrm{C_5Me_5}$ rings and the $\mathrm{PPh_3}$ ligand. The crowding between the latter and the $\mathrm{C_5Me_5}$ group bonded to Rh(2) accounts for the unusual ^{1}H chemical shift (δ 1.43) of the methyl protons of this ring. The normally observed shift for η-$\mathrm{C_5Me_5}$ protons is *ca.* δ 1.9, and it seems that the high-field shift observed in (6) is due to shielding by the phenyl rings. This steric interaction produces interesting effects in the solid-state structure. Comparison of the angle ξ (see ref. 3 and Figure 3 for definition of the angles referred to herein) at Rh(1) (155°) and Rh(2) (149°) shows that the ring attached to Rh(2) has been repelled towards Rh(1) by the $\mathrm{PPh_3}$ group. It is also significant that C(11'), C(12'), and C(15'), the closest methyl substituents to the $\mathrm{PPh_3}$ ligand, show the greatest deviation from the plane of their $\mathrm{C_5}$ ring. It is commonly observed [30] in $\mathrm{C_5Me_5}$ complexes that the Me substituents bend away from the metal, and theoretical studies [2] trace this phenomenon to maximization of overlap of ring orbitals with the appropriate orbitals of the metal. In addition to this electronic effect it has been shown that intramolecular crowding increases the deviation from the plane.[31,32] Perhaps the most dramatic effect of the steric interaction between the $\mathrm{PPh_3}$ and η-$\mathrm{C_5Me_5}$ ligands is the lengthening of the Pt–Rh(2) bond [2.691(2) Å]

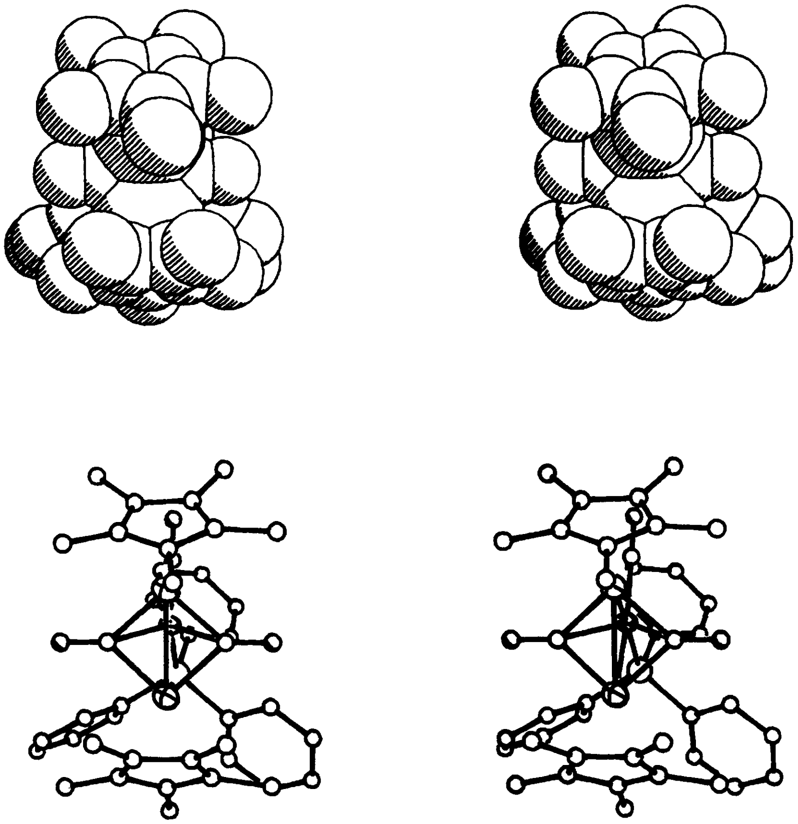
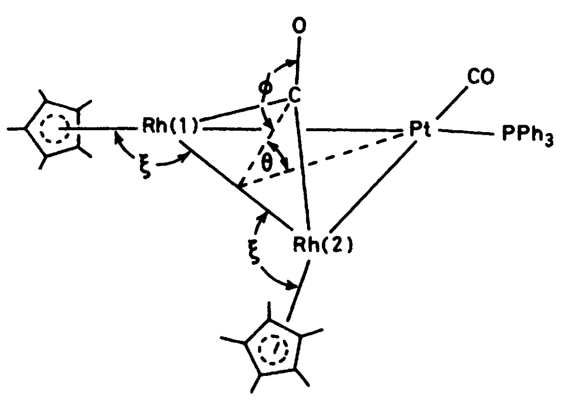


FIGURE 2 Stereoscopic views of the molecular structure of compound (6) in space-filling and conventional forms

compared with Pt–Rh(1) [2.618(2) Å]. It is interesting, in this context, to compare the structure of (6) with those of the two isoelectronic compounds [$Fe_2Pt(CO)_9(PPh_3)$] [33] and [$Co_2Pt(CO)_8(PPh_3)$].[34] For the iron complex, the Fe–Pt bond *trans* to the phosphine is longer (0.08 Å) than that *trans* to the carbonyl, and this was attributed to the higher *trans* influence of the PPh_3 group.[33] However, in the cobalt complex the Co–Pt bonds differ by only 0.01 Å, that *trans* to the phosphine being slightly shorter.



	Compound (6)	[$Rh_3(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2$]$^-$ Observed (ref. 38)	Calculated (ref. 3)
θ	79.8 (average of 78.0 and 81.5)	77.5	74
ξ	155.0 [Rh(1)] 149.2 [Rh(2)]	159.4	157
ϕ	169.6 (average of 169.3 and 169.9)	170	176

FIGURE 3 Comparison of certain angles (°) for complex (6) with observed and calculated angles for the anion [$Rh_3(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2$]$^-$

The Rh(1)–Rh(2) bond length [2.647(2) Å] is within the range (2.55—2.77 Å) found for similar single bonds in many Rh(η-C_5R_5) compounds.[35,36] The Rh–C(ring) distances in (6) average 2.26 Å, typical of those determined for other Rh^I(η-C_5Me_5) species.[37] The Pt–P and Pt–C(3) distances in (6) (Table 3) also are typical for such bonds.[27]

The two CO groups which bridge the Rh(1)–Rh(2) bond are semi-triply bridging to the platinum atom. This bonding mode was first noted for the anion [$Rh_3(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2$]$^-$ (ref. 38), and has more recently been found in the complexes [$Mo_2Pt_2(\mu\text{-}CO)_6(PEt_3)_2(\eta\text{-}C_5H_5)_2$] [39] and [$Co_2Pt(\mu\text{-}CO)(CO)_7(PPh_3)$].[34] In (6) the bridging CO ligands are 2.52 (mean) Å from the platinum and this may be compared with 2.69 (mean) Å in the dimolybdenumdiplatinum compound.

The bonding in [$Rh_3(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2$]$^-$ has been studied [3] using extended Hückel calculations, and it was found that, in correlating the bonding with the structure, the angles θ, ϕ, and ξ (Figure 3) are important variables. Calculated overlap populations indicated a significant interaction of the unique Rh atom with the bridging carbonyls, and this was traced to $Rh(CO)_2^-$ lone-pair interactions with bridging π^*(CO), and not charge transfer from carbonyl π orbitals to the 16-electron Rh centre. Bending back of the C_5H_5 rings (reducing ξ) was found to be inextricably coupled to reducing θ and ϕ, and this applies also to the complexes $[M_2(CO)_2(\eta\text{-}C_5H_5)_2]$ themselves.[24] The structure of (6) is fully consistent with the spectroscopic data, especially the observed $^{195}Pt-^{13}C$ coupling (125 Hz) involving the bridging carbonyls in the ^{13}C spectrum, and with the μ-CO stretch in the i.r. at *ca.* 21 cm^{-1} lower frequency than in $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$.

TABLE 2

Atomic positional (fractional co-ordinates) parameters for complex (6), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pt	0.202 48(5)	0.183 52(4)	0.196 66(4)
Rh(1)	0.245 97(10)	0.116 60(8)	0.338 50(7)
Rh(2)	0.435 43(9)	0.243 45(8)	0.280 35(7)
P	0.215 8(4)	0.270 6(3)	0.083 9(3)
C(1)	0.353 4(14)	0.085 3(12)	0.240 8(10)
O(1)	0.375 5(10)	0.008 5(8)	0.195 7(8)
C(2)	0.299 4(14)	0.277 2(12)	0.350 9(10)
O(2)	0.277 9(11)	0.353 6(8)	0.395 4(8)
C(3)	0.035(2)	0.113 8(13)	0.183 8(11)
O(3)	−0.073 9(11)	0.068 8(12)	0.170 7(9)
C(11)	0.596 9(11)	0.355 0(8)	0.229 0(6)
C(12)	0.587 2(11)	0.404 4(8)	0.319 1(6)
C(13)	0.609 6(11)	0.336 7(8)	0.373 3(6)
C(14)	0.633 1(11)	0.245 5(8)	0.316 7(6)
C(15)	0.625 3(11)	0.256 8(8)	0.227 6(6)
C(11′)	0.595(2)	0.402(2)	0.154 2(15)
C(12′)	0.567(2)	0.514 8(14)	0.360(2)
C(13′)	0.615(2)	0.359(2)	0.475 2(12)
C(14′)	0.665(2)	0.156(2)	0.347 3(14)
C(15′)	0.653(2)	0.184 7(15)	0.146 2(13)
C(21)	0.106 9(10)	−0.034 3(8)	0.353 9(7)
C(22)	0.072 9(10)	0.055 5(8)	0.403 8(7)
C(23)	0.170 8(10)	0.114 3(8)	0.472 9(7)
C(24)	0.265 3(10)	0.060 9(8)	0.465 7(7)
C(25)	0.225 8(10)	−0.031 0(8)	0.392 2(7)
C(21′)	0.026(3)	−0.123 2(15)	0.276 8(13)
C(22′)	−0.051(2)	0.076(2)	0.392 3(13)
C(23′)	0.164(3)	0.213(2)	0.543(2)
C(24′)	0.384(2)	0.095(3)	0.528 2(14)
C(25′)	0.296(3)	−0.108(2)	0.366(2)
C(32)	0.265 6(9)	0.230 2(8)	−0.097 1(7)
C(33)	0.323 0(9)	0.185 8(8)	−0.168 5(7)
C(34)	0.407 3(9)	0.129 2(8)	−0.154 6(7)
C(35)	0.434 2(9)	0.116 9(8)	−0.069 3(7)
C(36)	0.376 8(9)	0.161 3(8)	0.002 1(7)
C(31)	0.292 5(9)	0.217 9(8)	−0.011 8(7)
C(42)	−0.009 7(9)	0.151 5(7)	−0.013 8(7)
C(43)	−0.129 6(9)	0.133 6(7)	−0.054 6(7)
C(44)	−0.178 1(9)	0.220 3(7)	−0.052 4(7)
C(45)	−0.106 7(9)	0.324 9(7)	−0.009 5(7)
C(46)	0.013 2(9)	0.342 8(7)	0.031 3(7)
C(41)	0.061 7(9)	0.256 1(7)	0.029 1(7)
C(52)	0.339 5(10)	0.480 4(7)	0.062 3(5)
C(53)	0.382 8(10)	0.592 5(7)	0.093 0(5)
C(54)	0.370 9(10)	0.641 7(7)	0.180 7(5)
C(55)	0.315 6(10)	0.578 8(7)	0.237 8(5)
C(56)	0.272 3(10)	0.466 7(7)	0.207 1(5)
C(51)	0.284 2(10)	0.417 5(7)	0.119 4(5)
C	−0.050(12)	0.435(10)	0.285(9)
Cl(1)	−0.009(4)	0.376(3)	0.317(3)
Cl(2)	−0.037(5)	0.568(4)	0.259(3)

The molecular structure of (6), as determined by *X*-ray diffraction, confirmed that in its synthesis from $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ and $[Pt(C_2H_4)(PPh_3)_2]$ a PPh_3 group on platinum had been displaced by CO. This is a reactivity pattern observed in the preparation of several other tri- and tetra-nuclear metal complexes from this particular platinum(0) reagent.[40] In order to facilitate the transfer of CO from rhodium to platinum, the compound $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ was treated with $[Pt(C_2H_4)_2(PPh_3)]$ which is known to abstract CO (see below). Although (6) was isolated from this reaction there were several other products, in an apparently complex mixture. The major component was a thermally unstable red solid (7) [$\nu_{max.}$(CO) 1 670 cm^{-1}] which could not be isolated pure. Its ^1H n.m.r. spectrum showed resonances for η-C_5Me_5 and PPh_3 groups, and in addition a very broad resonance at δ 2.9 was indicative of co-ordinated C_2H_4.[41] In the ^{31}P spectrum there was a singlet resonance [δ 6.6 p.p.m., *J*(PtP) 3 697 Hz]. In the compound $[Pt(C_2H_4)_2(PPh_3)]$ the ^{31}P resonance [δ 25 p.p.m., to high frequency of 85% H_3PO_4(external)] has a similar $^{195}Pt-^{31}P$ coupling of 3 425 Hz.[41] On the basis of these data we propose the structure shown for (7). The reaction between (1) and $[Pt(C_2H_4)_2(PPh_3)]$ was also briefly studied, but it also afforded a complex mixture of products.

TABLE 3

Selected bond distances (Å) and angles (°) for $[PtRh_2(\mu_3\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$ (6), with estimated standard deviations in parentheses

(*a*) Distances

Pt–Rh(1)	2.618(2)	Rh(1)–C(21)	2.242(9)
Pt–Rh(2)	2.691(2)	Rh(1)–C(22)	2.254(10)
Rh(1)–Rh(2)	2.647(2)	Rh(1)–C(23)	2.272(10)
Pt–C(1)	2.56(2)	Rh(1)–C(24)	2.272(11)
Rh(1)–C(1)	2.005(15)	Rh(1)–C(25)	2.253(11)
Rh(2)–C(1)	1.988(13)	Rh(2)–C(11)	2.292(10)
C(1)–O(1)	1.19(2)	Rh(2)–C(12)	2.274(0)
Pt–C(2)	2.476(13)	Rh(2)–C(13)	2.248(9)
Rh(1)–C(2)	2.013(15)	Rh(2)–C(14)	2.252(12)
Rh(2)–C(2)	2.00(2)	Rh(2)–C(15)	2.279(12)
C(2)–O(2)	1.18(2)	C(21)–C(21′)	1.53(2)
Pt–P	2.285(4)	C(22)–C(22′)	1.50(3)
P–C(31)	1.835(10)	C(23)–C(23′)	1.52(3)
P–C(41)	1.832(11)	C(24)–C(24′)	1.51(3)
P–C(51)	1.833(9)	C(25)–C(25′)	1.44(4)
Pt–C(3)	1.83(2)	C(11)–C(11′)	1.43(3)
C(3)–O(3)	1.19(2)	C(12)–C(12′)	1.54(3)
C–Cl(1) [a]	1.2(2)	C(13)–C(13′)	1.53(2)
C–Cl(2) [a]	1.9(2)	C(14)–C(14′)	1.49(3)
C–C [b]	1.420	C(15)–C(15′)	1.50(2)
C–C (Ph)	1.395		

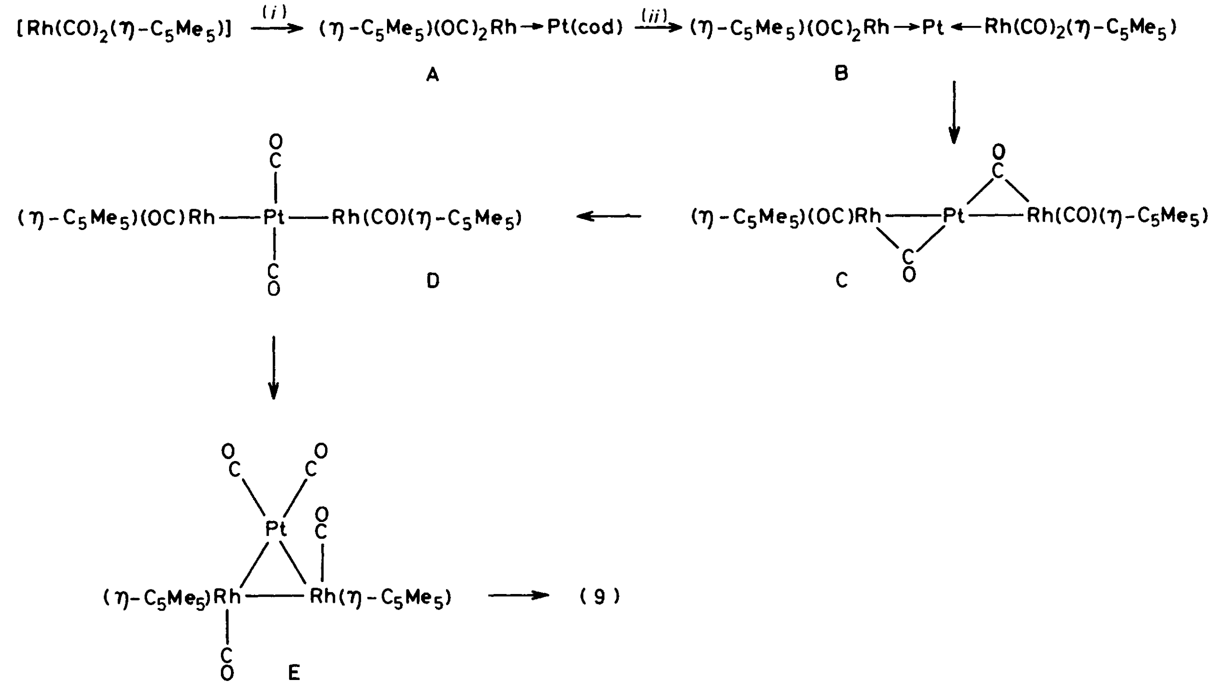
(*b*) Angles

Rh(1)–Pt–Rh(2)	59.8(1)	Rh(1)–Pt–C(3)	93.3(6)
Pt–Rh(1)–Rh(2)	61.5(1)	Rh(2)–Pt–P	105.7(1)
Pt–Rh(2)–Rh(1)	58.7(1)	C(3)–Pt–P	101.2(6)
Pt–C(1)–Rh(1)	68.8(5)	Pt–C(3)–O(3)	176.3(15)
Pt–C(1)–Rh(2)	71.4(5)	Pt–P–C(31)	115.8(4)
Rh(1)–C(1)–Rh(2)	83.0(5)	Pt–P–C(41)	112.2(4)
Pt–C(1)–O(1)	126.8(11)	Pt–P–C(51)	114.9(3)
Rh(1)–C(1)–O(1)	137.9(12)	C(31)–P–C(41)	101.1(5)
Rh(2)–C(1)–O(1)	137.3(11)	C(41)–P–C(51)	102.8(5)
Pt–C(2)–Rh(1)	70.5(4)	C(51)–P–C(31)	108.6(4)
Pt–C(2)–Rh(2)	73.1(4)	P–C(31)–C(32)	121.9(4)
Rh(1)–C(2)–Rh(2)	82.6(6)	P–C(41)–C(42)	116.6(3)
Pt–C(2)–O(2)	125.1(12)	P–C(51)–C(52)	123.4(3)
Rh(1)–C(2)–O(2)	137.1(12)	C–C–C [b]	108.0
Rh(2)–C(2)–O(2)	138.1(11)	C–C–C (Ph)	120.0

[a] In CH_2Cl_2 solvent. [b] In cyclopentadienyl ring.

A high-yield synthesis (90%) of (6) was found in the reaction of the mononuclear rhodium compound $[\mathrm{Rh(CO)_2(\eta\text{-}C_5Me_5)}]$ with $[\mathrm{Pt(C_2H_4)_2(PPh_3)}]$ in light petroleum at room temperature. A minor product of this reaction is $[\mathrm{Pt_3(\mu\text{-}CO)_3(PPh_3)_3}]$ (8). The preparation of (6) in this manner uses the principle developed earlier[27] with platinum compounds $[\mathrm{Pt(C_2H_4)_2(PR_3)}]$ functioning as CO-abstracting reagents from co-ordinatively saturated metal carbonyls, leading to metal–metal bond formation.

Compound (8) does not seem to have been previously reported although it is a member of a well established series of compounds, $[\mathrm{Pt_3(\mu\text{-}CO)_3(PR_3)_3}]$.[42,43] The ^{31}P n.m.r. spectrum at room temperature showed a broad resonance (δ 53.3 p.p.m.), and addition of $\mathrm{PPh_3}$ enhanced the broadening. In contrast, when the spectrum was measured at −50 °C very sharp lines were observed centred at δ 54.9 p.p.m., the pattern of peaks being as found for other molecules of this type.[43] From the spectrum J(PtPt) was measured as 1 851 Hz, the largest yet reported for a species $[\mathrm{Pt_3(\mu\text{-}CO)_3(PR_3)_3}]$. The broad resonance seen at room temperature must be due to exchange with free $\mathrm{PPh_3}$, exchange most likely occurring *via* the known[42] compound $[\mathrm{Pt_3(\mu\text{-}CO)_3(PPh_3)_4}]$. Although this is the first report of this phenomenon in $[\mathrm{Pt_3(\mu\text{-}CO)_3(PR_3)_3}]$ complexes, n.m.r. studies[44] on the structurally related compound $[\mathrm{Pt_3(\mu\text{-}CNBu^t)_3(CNBu^t)_3}]$ have revealed $\mathrm{CNBu^t}$ exchange *via* ligand dissociation. The broad ^{31}P resonance recently reported[45] for $[\mathrm{Pt_3(\mu\text{-}CO)_3(PMe_3)_3}]$ is also probably due to $\mathrm{PMe_3}$ exchange in the presence of traces of free ligand.



Scheme 2 (*i*) + $[\mathrm{Pt(cod)_2}]$, − cod; (*ii*) + $[\mathrm{Rh(CO)_2(\eta\text{-}C_5Me_5)}]$, − cod

Compound (8) is also formed when (6) is treated with CO (1 bar).* The other products of this reaction are $[\mathrm{Rh(CO)_2(\eta\text{-}C_5Me_5)}]$ and the pentanuclear platinum cluster $[\mathrm{Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4}]$.[34,46]

Reaction between $[\mathrm{Rh(CO)_2(\eta\text{-}C_5Me_5)}]$ and $[\mathrm{Pt(cod)_2}]$ (2 : 1 mol ratio) proceeds with transfer of CO groups to platinum to give (90% yield) the compound $[\mathrm{PtRh_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5Me_5)_2}]$ (9), together with trace amounts of (5) and black $[\{\mathrm{Pt(CO)_2}\}_n]$. Complex (9) was also prepared in high yield by reacting $[\mathrm{Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2}]$ with $[\mathrm{Pt_2(CO)_2(\eta\text{-}C_5H_5)_2}]$. The fate of the $\mathrm{C_5H_5}$ groups in this reaction is not known.

Compound (9) is isoelectronic with the anion $[\mathrm{Rh_3(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2}]^-$ (ref. 38) and may be regarded as derived from the latter by isolobal replacement of $\mathrm{Rh(CO)_2}^-$ by $\mathrm{Pt(CO)_2}$. The i.r. spectrum of (9) shows CO stretching bands at 2 042, 1 999, and 1 745 cm^{-1}. The absorption due to the bridging CO ligands is at higher frequency than those in the spectra of compounds (5) (1 708 cm^{-1}) and (6) (1 711 cm^{-1}) and this probably reflects a weaker interaction between the platinum and the bridging carbonyls in (9) than in (5) or (6). Moreover, from the ^{13}C n.m.r. spectrum of (9) the triplet resonance due to the bridging CO groups had a smaller ^{195}Pt–^{13}C coupling (72 Hz) than the corresponding couplings measured from the spectra of (5) (239 Hz) and (6) (125 Hz).

Formation of (9) from $[\mathrm{Pt(cod)_2}]$ and $[\mathrm{Rh(CO)_2(\eta\text{-}C_5Me_5)}]$ could proceed as indicated in Scheme 2. The intermediates A and B are reasonable in the context of theoretical treatments[4,47] of $[\mathrm{Co(CO)_2(\eta\text{-}C_5H_5)}]$ which show that the highest occupied molecular orbital of this molecule is to be regarded as a non-bonding electron pair at the metal, thus accounting for the existence of adducts

---

* Throughout this paper: 1 bar = 10^5 N m^{-2}.

such as $[(\eta\text{-}C_5H_5)(OC)_2Co{\rightarrow}HgCl_2]$.[48] Moreover, the 18-electron molecules $[M(PMe_3)_2(\eta\text{-}C_5H_5)]$ (M = Co or Rh) are strong donors, forming metal–metal donor bonds with various metal halides.[49] Indeed, intermediate B of Scheme 2 is isoelectronic with the recently isolated cation $[Ag\{Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)\}_2]^+$ (ref. 50) and is related to $[Pt\{P(cyclo\text{-}C_6H_{11})_3\}_2]$.[51] Transfer of two CO groups *via* complex C would give D, and subsequently (9) through the non-bridged intermediate E. It is unlikely that (9) is produced through the intermediacy of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ since the latter was not detected when following the reaction by i.r. spectroscopy, nor was its intense blue colour observed. Moreover, if the dirhodium species were involved the proportion of (5) in the product mixture would be expected to be greater. The formation of small amounts of (5) can be accounted for by reaction of (9) with the cod released from $[Pt(cod)_2]$.

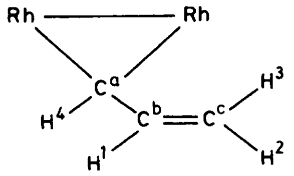
The reaction between $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ and $[Ni(cod)_2]$ was also investigated and found to afford a red-brown, thermally unstable, and extremely air-sensitive solid formulated as $[NiRh_2(\mu\text{-}CO)_2(cod)(\eta\text{-}C_5Me_5)_2]$ (10), though satisfactory microanalyses were not obtained. A field-desorption (f.d.) mass spectrum showed the expected molecular ion at 698, with the correct isotope pattern for nickel. The i.r. spectrum showed a CO stretch at 1 673 cm^{-1} suggesting the presence of a strongly triply-bridging carbonyl ligand. In the platinum analogue (5) the corresponding band is at 1 708 cm^{-1}. The ^1H n.m.r. had the expected peaks for C_5Me_5 and cod groups, and the ^{13}C spectrum showed the resonance for μ-CO at δ 253.7 [t, *J*(RhC) 46 Hz]. Compound (10) instantly decomposes on attempted chromatography on alumina or silica gel.

The salt $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][PF_6]$, which is isoelectronic with $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$, has recently been reported.[52] The reaction of the nitrosyldirhodium salt with $[Pt(cod)_2]$ was investigated, and gave a brown crystalline complex $[PtRh_2(\mu_3\text{-}CO)(\mu_3\text{-}NO)(cod)(\eta\text{-}C_5Me_5)_2][PF_6]$ (11), in which the cation is very probably structurally analogous to (5). The i.r. spectrum of (11) showed bands due to the CO and NO ligands at 1 762 and 1 495 cm^{-1}, respectively. The corresponding absorptions in the spectrum of the precursor $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][PF_6]$ occur at 1 853 and 1 533 cm^{-1}, respectively. The ^{13}C n.m.r. spectrum of (11) had the expected triplet resonance for the μ-CO ligand [δ 234.3 p.p.m., with *J*(RhC) 46 Hz]. However, both the ^1H and ^{13}C n.m.r. data, obtained at room temperature, revealed that (11) is undergoing dynamic behaviour since the CH and CH_2 groups of the cod ligand each gave rise to only one signal.

EXPERIMENTAL

The ^1H, $^{13}C\text{-}\{^1H\}$, $^{31}P\text{-}\{^1H\}$, ^{19}F, and $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectra were measured in $[^2H_1]$chloroform on JNM PS-100, FX 90Q, or FX 200 spectrometers, as appropriate. Data given are for room-temperature measurements unless otherwise stated and coupling constants are in Hz. Carbon-13 chemical shifts are relative to $SiMe_4$ with positive values to high frequency of the reference. Phosphorus-31 chemical shifts are relative to 85% H_3PO_4 (external), ^{19}F relative to CCl_3F (external) and both are positive to high frequency of the reference. The ^{195}Pt shifts (δ) are measured to high frequency of $\Xi(^{195}Pt) = 21.4$ MHz. Tris(acetylacetonato)chromium(III) was added to reduce relaxation times. Molecular weights were determined from f.d. mass spectra measured on an A.E.I. MS902 instrument, and i.r. spectra on a Perkin-Elmer 257 spectrometer. All reactions were carried out in Schlenk tubes under an atmosphere of dry oxygen-free nitrogen, using freshly distilled solvents. Light petroleum refers to that fraction of b.p. 30—40 °C. Chromatography was on alumina columns. The complex $[Rh_2Cl_2(\mu\text{-}Cl)_2(\eta\text{-}C_5Me_5)_2]$ was prepared by refluxing $RhCl_3\cdot 3H_2O$ in methanol with C_5Me_5H,[53] and converted to $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ by a modification of the published method;[54] this involved extraction with light petroleum instead of sublimation of the reaction mixture. Established methods were used to prepare $[Pt(cod)_2]$,[55] $[Pt(C_2H_4)(PPh_3)_2]$,[10] $[Pt(C_2H_4)_2(PPh_3)]$,[10] $[Pt_2(CO)_2(\eta\text{-}C_5H_5)_2]$,[56] $[Ni(cod)_2]$,[57] CH_2N_2,[58] $(CH_2{=}CH)HCN_2$,[59] and $(CF_3)_2CN_2$.[60]

Reactions involving the Diazoalkanes.—Blue solutions of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (*ca.* 0.5 mmol) in dichloromethane or diethyl ether (10 cm^3) were treated dropwise with diethyl ether solutions (5—10 cm^3) of the diazoalkanes in slight excess at 0—20 °C. The red solutions obtained were evaporated and the residues extracted with light petroleum. Filtration of the extracts and removal of solvent afforded, in 90—95% yield, red *crystals* (Table 1) of the complexes $[Rh_2(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5Me_5)_2]$ (1) {n.m.r.: ^1H, δ 5.92 (m, 2 H, CH_2) and 1.92 (s, 30 H, C_5Me_5); $^{13}C\text{-}\{^1H\}$, δ 196.5 [t, CO, *J*(RhC) 44], 111.2 [t, CH_2, *J*(RhC) 30, off-resonance decoupling gives *J*(HC) 144], 100.1 [d, C_5Me$_5$, *J*(RhC) 3], and 10.7 p.p.m. (s, C_5*Me*$_5$); $^{13}C\text{-}\{^1H\}$ (−40 °C), δ 196.5 [d, CO, *J*(RhC) 88], 111.2 [t, CH_2, *J*(RhC) 30], 100.1 [d, C_5Me$_5$, *J*(RhC) 3], and 10.7 p.p.m. (s, C_5*Me*$_5$)}, $[Rh_2\{\mu\text{-}C(CF_3)_2\}(CO)_2(\eta\text{-}C_5Me_5)_2]$ (2) {n.m.r.: ^1H, δ 1.92 (s, 30 H, C_5Me_5); ^{19}F, δ −49.26 [m, 6 F, CF_3, *J*(RhF) 2]}, $[Rh_2\{\mu\text{-}CH(CO_2Et)\}(CO)_2(\eta\text{-}C_5Me_5)_2]$ (3) {n.m.r.: ^1H, δ 5.78 [t, 1 H, C*H*CO$_2$Et, *J*(RhH) 2], 4.08 [q, 2 H, CH_2, *J*(HH) 7], 1.90 (s, 30 H, C_5Me_5), 1.24 [t, 3 H, CH$_2$*Me*, *J*(HH) 7]; $^{13}C\text{-}\{^1H\}$, δ, 196.2 [t, CO, *J*(RhC) 44], 195.9 [t, CO, *J*(RhC) 44], 179.7 (*C*O$_2$Et), 106.3 [t, *C*CO$_2$Et, *J*(RhC) 32], 100.5 (*C*$_5$Me$_5$), 59.4 (CH_2), 14.9 (CH$_2$*Me*), and 10.3 p.p.m. (C$_5$*Me*$_5$); $^{13}C\text{-}\{^1H\}$ (−90 °C), δ 195.5 [d, CO, *J*(RhC) 88], 195.4 [d, CO, *J*(RhC) 88], 178.3 (*C*O$_2$Et), 105.1 [t, *C*CO$_2$Et, *J*(RhC) 32], 99.4 (br, *C*$_5$Me$_5$), 59.3 (CH_2), 13.8 (CH$_2$*Me*), 9.8 (C$_5$*Me*$_5$), and 9.4 p.p.m. (C$_5$*Me*$_5$)}, and $[Rh_2\{\mu\text{-}CH(CH{=}CH_2)\}(CO)_2(\eta\text{-}C_5Me_5)_2]$ (4) {n.m.r.: ^1H, δ 6.64 [d, 1 H, H^4, $J(H^4H^1)$ 12], 6.33 [d of d of d, 1 H, H^1, $J(H^1H^2)$ 10, $J(H^1H^3)$ 15, $J(H^1H^4)$ 12], 4.67 [d of d, 1 H, H^3, $J(H^3H^1)$ 15, $J(H^3H^2)$ 3], 4.51 [d of d, 1 H, H^2, $J(H^2H^1)$ 10, $J(H^2H^3)$ 3], and 1.95 (s, 30 H, C$_5$*Me*$_5$); $^{13}C\text{-}\{^1H\}$, δ 196.9 (m, br, CO), 156.4 (C^b), 127.2 [t, C^a, *J*(RhC) 29], 100.4 (*C*$_5$Me$_5$) and 10.3 p.p.m. (C$_5$*Me*$_5$)}.



Reactions of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ *with Low-valent Platinum Compounds.*—(*a*) The compound $[Pt(cod)_2]$ (0.100 g, 0.243 mmol) was added to a stirred solution of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (0.130 g, 0.243 mmol) in dichloromethane (5 cm^3) at room temperature. After 10 min, volatiles were removed *in vacuo* and the residue dissolved in light petroleum (10 cm^3) and chromatographed. A yellow-brown band was eluted with light petroleum–dichloromethane (3 : 1). Removal of solvent afforded yellowish brown *crystals* of $[PtRh_2(\mu\text{-}CO)_2(cod)(\eta\text{-}C_5Me_5)_2]$ (5) (0.190 g, 94%) [Found: C, 43.7; H, 5.5; *M*(f.d.) 835. $C_{30}H_{42}O_2PtRh_2$ requires C, 43.1; H, 5.1%; *M* 835]; $\nu_{max.}$(CO) (hexane), 1 708s cm^{-1}. N.m.r.: ^1H, δ 4.92 [m, 4 H, CH, *J*(PtH) 72] and 1.88 (m, 38 H, CH_2 and Me); $^{13}C\text{-}\{^1H\}$, δ 251.5 [t, CO, *J*(RhC) 44, *J*(PtC) 239], 98.7 (C_5Me$_5$), 86.8 [CH, *J*(PtC) 111], 30.4 [CH_2, *J*(PtC) 10], and 9.5 p.p.m. (C_5Me_5); $^{195}Pt\text{-}\{^1H\}$, δ 934 p.p.m.

(*b*) A mixture of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (0.266 g, 0.50 mmol) and $[Pt_2(CO)_2(\eta\text{-}C_5H_5)_2]$ (0.288 g, 0.50 mmol) in dichloromethane (10 cm^3) was stirred (2 h) at room temperature. Solvent was removed *in vacuo*, and the residue dissolved in light petroleum (20 cm^3) and chromatographed. Elution with light petroleum–CH_2Cl_2 (2 : 1) separated a yellow-brown band. Removal of solvent afforded orange-brown *crystals* of $[PtRh_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5Me_5)_2]$ (9) (0.340 g, 87%) [Found: C, 37.0; H, 4.1; *M* (f.d.) 783. $C_{24}H_{30}O_4PtRh_2$ requires C, 36.8; H, 3.9%; *M* 783]; $\nu_{max.}$(CO) (hexane) 2 042s, 1 999s, and 1 745 cm^{-1}. N.m.r.: ^1H, δ 1.85 (s, 30 H, C_5Me_5); $^{13}C\text{-}\{^1H\}$, δ 248.0 [t, μ-CO, *J*(RhC) 44, *J*(PtC) 72] and 189.0 p.p.m. [CO, *J*(PtC) 1 858]; $^{195}Pt\text{-}\{^1H\}$, δ 51.8 p.p.m. [t, *J*(RhPt) 15].

(*c*) The compounds $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (0.106 g, 0.20 mmol) and $[Pt(C_2H_4)(PPh_3)_2]$ (0.149 g, 0.20 mmol) in diethyl ether (10 cm^3) were stirred (16 h) at room temperature. Solvent was removed and the residue extracted with light petroleum leaving a yellow solid $[\{Pt(PPh_3)_n\}]$ ($n = 3$—4) (95 mg). The extracts were reduced to 5 cm^3 and chromatographed. Elution with light petroleum–diethyl ether (1 : 1) gave orange-brown *crystals* of $[PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$ (6) (60 mg, 30%), followed by unreacted $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (50 mg, 47%).

In a similar reaction between $[Pt(C_2H_4)_2(PPh_3)]$ (0.205 g, 0.40 mmol) and $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (0.212 g, 0.40 mmol) in diethyl ether (10 cm^3), compound (6) was obtained (0.125 g) in 31% yield after light petroleum extraction of the residue. Spectroscopic data for (6) are given below. The major product of this reaction was the brown-red solid (0.160 g) residue after solvent removal. On the basis of the spectroscopic properties (see Discussion section) these *microcrystals* were formulated as $[PtRh_2(\mu\text{-}CO)_2(PPh_3)(C_2H_4)(\eta\text{-}C_5Me_5)_2]$ (7).

Reactions of $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ *with Low-valent Platinum Compounds.*—(*a*) A stirred solution of $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ (0.294 g, 1.00 mmol) in light petroleum (5 cm^3) was treated (30 min) with $[Pt(cod)_2]$ (0.205 g, 0.50 mmol). After removal of the volatile material *in vacuo*, the residue was dissolved in light petroleum (15 cm^3) and chromatographed giving compounds (9) (0.352 g, 90%) and (5) (20 mg, 5%).

(*b*) The compounds $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ (0.200 g, 0.68 mmol) and $[Pt(C_2H_4)_2(PPh_3)]$ (0.172 g, 0.34 mmol) in light petroleum (10 cm^3) were stirred (18 h) at room temperature. The mixture was filtered, and the residue extracted with light petroleum–diethyl ether (1 : 1). The filtrate and extracts were reduced to *ca.* 5 cm^3 and chromatographed. Elution with light petroleum gave a small amount of unreacted $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$. Further elution with light petroleum–diethyl ether (1 : 1) afforded orange-brown *crystals* of $[PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$ (6) (0.310 g, 90%) [Found: C, 48.7; H, 4.7; *M* (f.d.) 1 017. $C_{41}H_{45}O_3PPtRh_2$ requires C, 48.4; H, 4.5%; *M* 1 017]; $\nu_{max.}$(CO) (hexane) 2 002s and 1 711s cm^{-1}. N.m.r.: ^1H, δ 7.3 (m, 15 H, Ph), 1.92 (s, 15 H, C_5Me_5), and 1.43 (s, 15 H, C_5Me_5); $^{13}C\text{-}\{^1H\}$, δ 252.7 [t, μ-CO, *J*(RhC) 44, *J*(PtC) 125], 184.4 [d of d, CO, *J*(PtC) 1 810, *J*(RhC) *ca.* 10, 4], 133.9—128.2 (Ph), 99.8 (C_5Me$_5$), 9.7 (C_5Me_5), and 9.0 p.p.m. (C_5Me_5); $^{31}P\text{-}\{^1H\}$, δ 26.8 [d, *J*(RhP) 15, *J*(PtP) 4 004]; $^{195}Pt\text{-}\{^1H\}$, δ −5.8 p.p.m. [d of d of d, *J*(PPt) 4 004, *J*(RhPt) 27, 6].

The orange-brown powder remaining after solvent extraction gave *microcrystals* of $[Pt_3(\mu\text{-}CO)_3(PPh_3)_3]$ (8) (10 mg, 6%) (Found: C, 47.6; H, 3.6; P, 5.8. $C_{57}H_{45}O_3P_3Pt_3$ requires C, 47.0; H, 3.1; P, 6.4%); $\nu_{max.}$(CO) (Nujol) 1 843w, 1 799s, and 1 780s cm^{-1}. N.m.r.: ^1H, δ 7.4 (m, br, Ph); $^{31}P\text{-}\{^1H\}$, δ 53.3 (m, br); $^{31}P\text{-}\{^1H\}$ (−50 °C), δ 54.9 p.p.m. [m, *J*(PtPt′) 1 851, *J*(PtP) 4 919, *J*(PtP′) 459, *J*(PP′) 54].

Reaction Between $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ *and* $[Ni(cod)_2]$.—The compounds $[Ni(cod)_2]$ (0.062 g, 0.225 mmol) and $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (0.120 g, 0.225 mmol) in toluene (5 cm^3) were stirred (4 h) at room temperature. The purple-red mixture was filtered and the filtrate was evaporated to dryness giving a red-brown thermally unstable extremely air-sensitive solid (0.140 g) identified as $[NiRh_2(\mu\text{-}CO)_2(cod)(\eta\text{-}C_5Me_5)_2]$ (10) [*M* (f.d.) 698, $C_{30}H_{42}NiO_2Rh_2$ requires *M* 698]; $\nu_{max.}$(CO) (CH_2Cl_2) 1 673s cm^{-1}. N.m.r.: ^1H (in [$^2H_6$]benzene), δ 5.08 (br, 4 H, CH), 2.15 (s, 8 H, CH_2), and 1.80 (s, 30 H, C_5Me_5); $^{13}C\text{-}\{^1H\}$ (in [$^2H_8$]toluene), δ 253.7 [t, CO, *J*(RhC) 46], 97.2 (C_5Me$_5$), 89.3 (CH), 30.5 (CH_2), and 8.9 p.p.m. (C_5Me_5). Compound (10) decomposed instantly on attempted chromatography regenerating $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$.

Reaction Between $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][PF_6]$ *and* $[Pt(cod)_2]$.—Bis(cyclo-octa-1,5-diene)platinum (0.066 g, 0.16 mmol) was added to the dirhodium salt (0.100 g, 0.16 mmol) in CH_2Cl_2 (5 cm^3), the mixture changing rapidly from blue to yellowish brown. Volatiles were removed *in vacuo* and the residue crystallised from CH_2Cl_2–Et_2O to give brown *crystals* of $[PtRh_2(\mu_3\text{-}CO)(\mu_3\text{-}NO)(cod)(\eta\text{-}C_5Me_5)_2][PF_6]$ (0.138 g, 93%) (Found: C, 34.6; H, 4.4; N, 1.5. $C_{29}H_{42}F_6NO_2PPtRh_2$ requires C, 35.5; H, 4.3; N, 1.4%); $\nu_{max.}$ (Nujol) 1 762 (CO) and 1 495 (NO) cm^{-1}. N.m.r.: ^1H, δ 5.28 [m, br, 4 H, CH, *J*(PtH) 72], 2.04 (s, 8 H, CH_2), and 1.80 (s, 30 H, C_5Me_5); $^{13}C\text{-}\{^1H\}$, δ 234.3 [t, μ-CO, *J*(RhC) 46], 101.4 (C_5Me$_5$), 95.1 [CH, *J*(PtC) 114], 29.8 (CH_2), and 8.0 p.p.m. (C_5Me_5); $^{195}Pt\text{-}\{^1H\}$, δ 988.7 p.p.m. [t, *J*(RhPt) 21].

Crystal Structure Determination of $[Rh_2Pt(\mu_3\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$ (6).—Diffracted intensities were collected at 220 K from a crystal of dimensions 0.20 × 0.08 × 0.10 mm (mounted under nitrogen in a Lindemann glass tube) on a Nicolet $P2_1m$ four-circle diffractometer. Of the total 7 614 independent reflections for $2.9 \leqslant 2\theta \leqslant 50.0°$, only 4 285 satisfied the criterion $I \geqslant 3.0\sigma(I)$, indicating poor crystal quality; these were used in the solution and refinement of the structure. Three check reflections were used to monitor the stability of the measurements; these were remeasured every 48 reflections, and no significant variation was observed. The intensities were corrected for Lorentz, polarisation, and *X*-ray absorption effects.

Crystal data. $C_{41}H_{45}O_3PPtRh_2\cdot\frac{1}{8}CH_2Cl_2$, $M = 1\,027.5$, Triclinic, $a = 11.185(3)$, $b = 13.278(7)$, $c = 15.443(9)$ Å,

$\alpha = 102.98(5)$, $\beta = 92.18(4)$, $\gamma = 105.88(4)°$, $U = 2\,137(2)$ Å^3, D_m not measured, $Z = 2$, $D_c = 1.60$ g cm^{-3} (including solvent molecules), $F(000) = 1\,006.5$, space group $P\bar{1}$ (no. 2), Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 41.5 cm^{-1}.

The structure was solved by location of the Pt and Rh atoms from a Patterson synthesis, and all other non-hydrogen atoms by successive electron-density difference syntheses. Refinement was carried out using blocked-cascade least squares with atoms C(11)—C(15) and C(21)—C(25) held as rigid pentagons, atoms C(31)—C(36), C(41)—C(46), and C(51)—C(56) as rigid hexagons. Geometrically constrained atoms were given isotropic thermal motion, but for all other non-hydrogen atoms anisotropic thermal parameters were used. Hydrogen atoms were incorporated at calculated positions (C–H = 0.96 Å); the methyl groups were constrained to tetrahedral geometry, and all chemically equivalent atoms were ascribed a common isotropic thermal parameter. Evidence was found, from electron-density difference syntheses, of the presence of methylene chloride in the crystal structure at a population parameter of *ca.* $\frac{1}{8}$ molecule of solvent per molecule of complex. For the solvent molecule the hydrogen atoms were omitted. Refinement converged at R 0.056 (R' 0.058). Individual weights were ascribed according to the scheme $w = [\sigma^2(F_o) + 0.002|F_o|^2]^{-1}$, where $\sigma(F_o)$ is the standard deviation based on counting statistics only, and this gave a satisfactory weight analysis. A final difference synthesis showed peaks *ca.* 1.8 and −1.3 e Å^{-3} in the neighbourhood of the metal atoms but with no significant features elsewhere. All calculations were carried out within the laboratory on an 'Eclipse' Data General minicomputer with the 'SHELXTL' system of programs.[61] Scattering factors, corrections for anomalous dispersion, and all other X-ray data, were taken from ref. 62. The results are summarised in Tables 2 and 3. Observed and calculated structure factors, all hydrogen atom co-ordinates, all thermal parameters, a complete set of calculated bond lengths and angles, and the equations of least-squares planes from which the interplanar angles have been calculated, are given in Supplementary Publication No. SUP 23283 (39 pp.).*

We thank the S.E.R.C. for support and a research studentship (to R. M. M.), Dr. N. G. Connelly for electrochemical measurements on compound (6), and J. Payne for preparing the compound $[Rh_2(\mu\text{-}CO)(\mu\text{-}NO)(\eta\text{-}C_5Me_5)_2][PF_6]$.

[1/1823 *Received, 23rd November,* 1981]

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

REFERENCES

[1] A. Nutton and P. M. Maitlis, *J. Organomet. Chem.*, 1979, **166**, C21.

[2] M. Elian and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 1058; M. Elian, M. M. L. Chen, D. M. P. Mingos, and R. Hoffmann, *ibid.*, 1976, **15**, 1148; B. E. R. Schilling, R. Hoffmann, and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 1979, **101**, 585.

[3] A. R. Pinhas, T. A. Albright, P. Hofmann, and R. Hoffmann, *Helv. Chim. Acta*, 1980, **63**, 29.

[4] P. Hofmann, *Angew. Chem. Int. Ed. Engl.*, 1979, **18**, 554.

[5] W. A. Herrmann, C. Krüger, R. Goddard, and I. Bernal, *J. Organomet. Chem.*, 1977, **140**, 73.

[6] N. M. Boag, M. Green, R. M. Mills, G. N. Pain, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1980, 1171.

[7] T. V. Ashworth, M. J. Chetcuti, L. J. Farrugia, J. A. K. Howard, J. C. Jeffery, R. M. Mills, G. N. Pain, F. G. A. Stone, and P. Woodward, 'Reactivity of Metal–Metal Bonds,' *Am. Chem. Soc., Symp. Ser.*, No. 155, 1981, pp. 299—313.

[8] W. A. Herrmann, C. Bauer, J. Plank, W. Kalcher, D. Speth, and M. L. Ziegler, *Angew. Chem. Int. Ed. Engl.*, 1981, **20**, 193.

[9] A. D. Clauss, P. A. Dimas, and J. R. Shapley, *J. Organomet. Chem.*, 1980, **201**, C31.

[10] T. V. Ashworth, J. A. K. Howard, M. Laguna, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1593; T. V. Ashworth, M. Berry, J. A. K. Howard, M. Laguna, and F. G. A. Stone, *ibid.*, p. 1615.

[11] A. F. Hegarty, in 'Chemistry of Diazonium and Diazo Groups,' Part 2, ed. S. Patai, Wiley, New York, 1978, ch. 12.

[12] L. Messerle and M. D. Curtis, *J. Am. Chem. Soc.*, 1980, **102**, 7789; M. D. Curtis, L. Messerle, N. A. Fotinos, and R. F. Gerlach, 'Reactivity of Metal–Metal Bonds,' *Am. Chem. Soc., Symp. Ser.*, No. 155, 1981, pp. 221—253.

[13] R. D. Adams and F. A. Cotton, 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975, ch. 12.

[14] L. J. Todd, J. R. Wilkinson, M. D. Rausch, S. A. Gardner, and R. S. Dickson, *J. Organomet. Chem.*, 1975, **101**, 133; R. S. Dickson, C. Mok, and G. Pain, *ibid.*, 1979, **166**, 385.

[15] R. S. Dickson and G. N. Pain, *J. Chem. Soc., Chem. Commun.*, 1979, 277.

[16] S. Shaik, R. Hoffmann, C. R. Fisel, and R. H. Summerville, *J. Am. Chem. Soc.*, 1980, **102**, 4555.

[17] M. P. Brown, J. R. Fisher, R. J. Puddephatt, and K. R. Seddon, *Inorg. Chem.*, 1979, **18**, 2808.

[18] R. S. Dickson and G. N. Pain, unpublished work.

[19] W. A. Herrmann, J. M. Huggins, B. Reiter, and C. Bauer, *J. Organomet. Chem.*, 1981, **214**, C19.

[20] W. A. Herrmann and C. Bauer, *J. Organomet. Chem.*, 1981, **204**, C21.

[21] M. Green, D. R. Hankey, M. Murray, A. G. Orpen, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1981, 689.

[22] W. A. Herrmann, *Adv. Organomet. Chem.*, 1982, **20**, 159.

[23] T. A. Albright, R. Hoffmann, J. C. Thibeault, and D. L. Thorn, *J. Am. Chem. Soc.*, 1979, **101**, 3801.

[24] A. R. Pinhas and R. Hoffmann, *Inorg. Chem.*, 1979, **18**, 654; E. D. Jemmis, A. R. Pinhas, and R. Hoffmann, *J. Am. Chem. Soc.*, 1980, **102**, 2576.

[25] M. L. Aldridge, M. Green, J. A. K. Howard, G. N. Pain, S. J. Porter, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 1333.

[26] J. A. K. Howard, J. C. Jeffery, M. Laguna, R. Navarro, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1981, 751.

[27] L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 1134.

[28] M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 1974, 2276.

[29] M. T. Chicote, M. Green, J. L. Spencer, F. G. A. Stone, and J. Vicente, *J. Chem. Soc., Dalton Trans.*, 1979, 536.

[30] L. R. Byers and L. F. Dahl, *Inorg. Chem.*, 1980, **19**, 277 and refs. therein.

[31] T. C. McKenzie, R. D. Sanner, and J. E. Bercaw, *J. Organomet. Chem.*, 1975, **102**, 457.

[32] A. Nutton, P. M. Bailey, and P. M. Maitlis, *J. Organomet. Chem.*, 1981, **213**, 313.

[33] R. Mason, J. Zubieta, A. T. T. Hsieh, J. Knight, and M. J. Mays, *J. Chem. Soc., Chem. Commun.*, 1972, 200.

[34] R. Bender, P. Braunstein, J. Fischer, L. Ricard, and A. Mitschler, *Nouv. J. Chim.*, 1981, **5**, 81.

[35] W. A. Herrmann, J. Plank, D. Riedel, M. L. Ziegler, K. Weidenhammer, E. Guggolz, and B. Balbach, *J. Am. Chem. Soc.*, 1981, **103**, 63.

[36] Trinh-Toan, K. W. Broach, S. A. Gardner, M. D. Rausch, and L. F. Dahl, *Inorg. Chem.*, 1977, **16**, 279 and refs. therein.

[37] P. M. Maitlis, *Chem. Soc. Rev.*, 1981, **10**, 1.

[38] W. D. Jones, M. A. White, and R. G. Bergman, *J. Am. Chem. Soc.*, 1978, **100**, 6770.

[39] R. Bender, P. Braunstein, Y. Dusansoy, and J. Protas, *J. Organomet. Chem.*, 1979, **172**, C51.

[40] L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 1274.

[41] N. C. Harrison, M. Murray, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1978, 1337.

[42] J. Chatt and P. Chini, *J. Chem. Soc. A*, 1970, 1538.

[43] A. Moor, P. S. Pregosin, and L. M. Venanzi, *Inorg. Chim. Acta*, 1981, **48**, 153 and refs. therein.

[44] M. Green, J. A. K. Howard, M. Murray, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1977, 1509.

[45] M. Berry, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1601; M. Berry, J. M. Gill, J. A. K. Howard, *ibid.*, 1980, 1625.

[46] J-P. Barbier, R. Bender, P. Braunstein, J. Fischer, and L. Ricard, *J. Chem. Res.* (*S*), 1978, 230, (*M*) 2913.

[47] A. Albright and R. Hoffmann, *Chem. Ber.*, 1978, **111**, 1578.

[48] I. W. Nowell and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1972, 2393.

[49] D. Dey and H. Werner, *Chem. Ber.*, 1979, **112**, 823; H. Werner, R. Feser, and W. Buchner, *ibid.*, p. 834.

[50] N. G. Connelly, A. R. Lucy, and A. M. R. Galas, *J. Chem. Soc., Chem. Commun.*, 1981, 43.

[51] J. Fornies, M. Green, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1977, 1006.

[52] S. Clamp, N. G. Connelly, and J. D. Payne, *J. Chem. Soc., Chem. Commun.*, 1981, 673.

[53] R. S. Threlkel and J. E. Bercaw, *J. Organomet. Chem.*, 1977, **136**, 1.

[54] J. W. Kang and P. M. Maitlis, *J. Organomet. Chem.*, 1971, **26**, 393.

[55] J. L. Spencer, *Inorg. Synth.*, 1979, **19**, 213.

[56] N. M. Boag, unpublished work.

[57] R. A. Schunn, *Inorg. Synth.*, 1974, **15**, 5.

[58] A. I. Vogel, 'Textbook of Practical Organic Chemistry,' 3rd edn., Longmans, London, 1964, p. 971.

[59] R. G. Salomon, M. F. Salomon, and T. R. Heyne, *J. Org. Chem.*, 1975, **40**, 756.

[60] D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.*, 1966, **88**, 3617.

[61] G. M. Sheldrick, SHELXTL programs for use with the Nicolet *X*-Ray System, Cambridge, 1976.

[62] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.