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Novel chemistry of rhodium induced by a new type of ligand, a phosphino-*N*-benzoylhydrazone: crystal structure of $[Rh(CO)\{C(CO_2Me){=}CHCO_2Me\}\{PPh_2CH[C(CO_2Me){=}C(CO_2Me)]C(Bu^t){=}N{-}N{=}C(Ph)O\}]$

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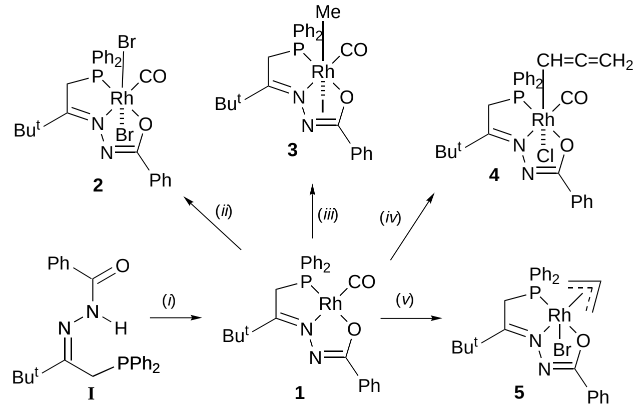
Treatment of the phosphino-*N*,*N*-dimethylhydrazone Z-$PPh_2CH_2C(Bu^t){=}NNMe_2$ with benzohydrazide in the presence of acetic acid gave the phosphino-*N*-benzoylhydrazone $PPh_2CH_2C(Bu^t){=}NNHC({=}O)Ph$ **I**. Treatment of the phosphine **I** with 0.5 equivalent of $[\{RhCl(CO)_2\}_2]$ gave the rhodium(I) complex $[Rh(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Ph)O\}]$ **1** containing two fused five-membered chelate rings. Complex **1** readily reacted with Br_2 to give the dibromorhodium(III) complex $[RhBr_2(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Ph)O\}]$ **2**. Similarly, it underwent oxidative-addition reactions with MeI or $HC{\equiv}CCH_2Cl$ to give rhodium(III) complexes of type $[RhX(R)(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Ph)O\}]$ (R = Me, X = I **3**; R = $CH{=}C{=}CH_2$, X = Cl **4**). In contrast, treatment of **1** with allyl bromide caused loss of the carbon monoxide ligand to give the η^3-allylrhodium(III) complex $[RhBr(\eta\text{-}3\text{-}C_3H_5)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Ph)O\}]$ **5**. Treatment of **1** with $MeO_2CC{\equiv}CCO_2Me$ gave the cyclometallated alkenylrhodium(III) complex $[Rh(CO)\{C(CO_2Me){=}CHCO_2Me\}\{PPh_2CH[C(CO_2Me){=}C(CO_2Me)]C(Bu^t){=}N{-}N{=}C(Ph)O\}]$ **6**, in which the phosphine ligand is tetradentate through *P*, *N*, *O* and *C*; in the formation of **6** one alkyne has attacked the methylene carbon of the phosphine ligand and the second has added to Rh−H to give $RhC(CO_2Me){=}CH(CO_2Me)$. On the prolonged heating **6** isomerised to give the rhodium(III) complex **7**; in this isomer the $C(CO_2Me){=}CH(CO_2Me)$ ligand is *trans* to phosphorus whereas in **6** it is *cis*. The crystal structure of **6** has been determined.

The direct synthesis of hydrazones $R^1R^2C({=}NNH_2)$ from a ketone and hydrazine is often difficult since an azine $R^1R^2C{=}N{-}N{=}CR^1R^2$ may form preferentially. A method of synthesizing hydrazones $R^1R^2C({=}NNH_2)$ was devised by Newkome and Fishel[1] which was to make the *N*,*N*-dimethylhydrazone $R^1R^2C({=}NNMe_2)$ first and then to carry out an exchange reaction with hydrazine using acid as catalyst. We have used this approach to synthesize the phosphino hydrazone Z-$PPh_2CH_2C(Bu^t){=}NNH_2$ by heating the readily prepared Z-$PPh_2CH_2C(Bu^t){=}NNMe_2$ with hydrazine in the presence of acetic acid as catalyst.[2] The compound Z-$PPh_2CH_2C(Bu^t){=}NNH_2$ and its derivatives have a very extensive chemistry.[2–12]

Hydrazides of carboxylic acids, *viz*. of type $RCONHNH_2$, are readily prepared and available and we reasoned that such hydrazides might also effect acid-catalysed displacement of H_2NNMe_2 from $PPh_2CH_2C(Bu^t){=}NNMe_2$ to give (diphenylphosphino)acylhydrazones of type $PPh_2CH_2C(Bu^t){=}NNHC({=}O)R$, which would show interesting properties as ligands. Some acylhydrazones[13–15] have been used as ligands, *e.g.* for Cu^{II},[13] Fe^{III}[14] and Sn^{IV},[15] but none of these contained a tertiary phosphine moiety. We thought that the monodeprotonated form of the (diphenylphosphino)acylhydrazone, *viz*. of type $PPh_2CH_2C(Bu^t){=}N{-}N{=}C(R)O^-$, might act as a terdentate ligand co-ordinating through *P*, *N* and *O*. We also thought that breakage of the oxygen–metal bond of the chelate might occur rapidly and reversibly and that the resultant bidentate ligand complexes show some interesting organometallic/co-ordination chemistry. We are finding this to be the case and in this paper we describe the synthesis of the new compound $PPh_2CH_2C(Bu^t){=}NNHC({=}O)Ph$ and some chemistry generated from it with rhodium-(I) and -(III) carbonyls.

Results and Discussion

The phosphino-*N*-benzoylhydrazone $PPh_2CH_2C(Bu^t){=}NNHC({=}O)Ph$ **I** was prepared by heating the phosphino-*N*,*N*-dimethylhydrazone Z-$PPh_2CH_2C(Bu^t){=}NNMe_2$[2] with an excess of benzohydrazide $NH_2NHC({=}O)Ph$ in hot ethanol for several hours in the presence of acetic acid as catalyst. We have used this compound to generate new chemistry from rhodium carbonyls and the various reactions of **I** and of the rhodium complexes are summarised in Schemes 1 and 2. Characterising microanalytical and mass spectral data are in the Experimental section, IR and $^{31}P\text{-}\{^1H\}$ NMR data are in Table 1, ^1H NMR data in Table 2, and selected $^{13}C\text{-}\{^1H\}$ NMR data in the Experimental section. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **I** showed a singlet at δ −22.4 and the IR spectrum showed bands at 3165 and 1665 cm^{-1} for ν(N−H) and ν(C=O), respectively.[15] The proton resonance at δ 9.57 was assigned to the NH proton which exchanged with D_2O. We suggest that this phosphine **I** has the *Z* configuration around the C=N bond, as do the phosphinohydrazones of type $PPh_2CH_2C(Bu^t){=}NNR_2$, R = H or Me.[2]



Scheme 1 (*i*) 0.5 equivalent $[\{RhCl(CO)_2\}_2]$; (*ii*) Br_2; (*iii*) MeI; (*iv*) propargyl chloride; (*v*) allyl bromide

We reasoned that treatment of the very substitution-labile rhodium(I) carbonyl complex $[Rh_2Cl_2(CO)_4]$[16] with **I** (1 equivalent per rhodium atom) ought to give a neutral rhodium(I) carbonyl complex in which the monodeprotonated **I** would bind to the rhodium as a terdentate ligand. Indeed in dichloromethane solution at 20 °C evolution of carbon monoxide occurred and the hoped for rhodium(I) complex $[Rh(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Ph)O\}]$ **1** was obtained Characterising microanalytical, mass and NMR spectral data are in the Experimental section and Tables 1 and 2. In the IR spectrum there was a strong band at 1974 cm^{-1} due to ν(C≡O), a value typical of a rhodium(I) carbonyl.[4,10,17] In the $^{31}P\text{-}\{^1H\}$ NMR spectrum the high value of $^1J(RhP) = 165$ Hz is typical for phosphorus co-ordinated to rhodium(I) and *trans* to a co-ordinated oxygen (an electronegative donor atom).[10,18,19] In the ^1H NMR spectrum (Table 2), the resonance of the CH_2P protons was a doublet at δ 3.99 with $^2J(PH) = 10.7$ Hz. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum the resonance of the C≡O ligand was a doublet of doublets at δ 191.7 with $^2J(PC) = 19.1$ and $^1J(RhC) = 72.2$ Hz, typical values for Rh−C≡O.[4,10] The chemical shift of the methylene carbon (CH_2P), δ 47.9 with $^1J(PC) = 29.9$ Hz, is typical of a methylene carbon in a five-membered chelate ring.[3,20] In six-membered chelate rings involving azine or hydrazone phosphine–metal complexes methylene carbons absorb at *ca.* δ 25.[3,4,8–11,20] In forming the two five-membered chelate rings isomerisation around the C=N bond from *Z* to *E* has occurred. We have found such isomerisation to be common in azine or hydrazone phosphine–metal complexes.[2,3,20–22]

A reaction of some rhodium(I)–tertiary phosphine complexes is oxidative addition to give rhodium(III)–tertiary phosphine complexes. However, rhodium(I) shows less tendency to undergo oxidative addition than does iridium(I), for example *trans*-$[RhCl(CO)(PPh_3)_2]$ has less tendency to undergo oxidative addition than does the well known *trans*-$[IrCl(CO)(PPh_3)_2]$.[17,23,24] We have investigated the behaviour of **1** towards oxidative addition. A solution of it in dichloromethane reacted immediately with bromine (in approximately two-fold excess) to give a single product (as evidenced by the $^{31}P\text{-}\{^1H\}$ NMR spectrum). We formulate this as $[RhBr_2(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Ph)O\}]$ **2**. In the ^1H NMR spectrum (Table 2) the methylene protons were equivalent as were the two sets of PPh_2 hydrogens, *i.e.* the two bromine atoms have added *trans*. The ν(C≡O) value of 2097 cm^{-1} is similar to values reported for rhodium(III) carbonyl complexes.[17,24]

Methyl iodide also added to complex **1** to give a single product which we formulate as having the stereochemistry **3**. The characterising proton NMR data in Table 2 show non-equivalent methylene hydrogens. The $RhCH_3$ hydrogens in the $^1H\text{-}\{^{31}P\}$ NMR spectrum were coupled to rhodium, $^2J(RhCH_3) = 2.2$ Hz and in the $^{13}C\text{-}\{^1H\}$ NMR spectrum the resonance of the RhMe carbon was a doublet of doublets at δ 16.7, $^2J(PC) = 2.8$ and $^1J(RhC) = 19.9$ Hz. The carbonyl carbon gave a doublet of doublets at δ 187.0, $^1J(RhC) = 58.4$ Hz, and the relatively small value of $^2J(PC) = 13.8$ Hz showed that the carbonyl ligand was *cis* to P. It is well established that addition of MeI usually goes so that the methyl and iodide ligands finish up mutually *trans* in the adducts of tertiary phosphine complexes of Rh^I, Ir^I and Pt^{II} and we tentatively formulate our adduct as having stereochemistry **3**.

Oxidative addition of propargyl (prop-2-ynyl) chloride ($HC{\equiv}CCH_2Cl$) to iridium(I) usually gives allenyl complexes containing a moiety $CH_2{=}C{=}CHM$ (M = metal), *i.e.* nucleophilic attack by the metal presumably occurs at the H*C*≡C carbon and not at the CH_2Cl carbon.[10,25,26] Such an addition to give an allenic complex **4** occurred when we treated **1** with $HC{\equiv}CCH_2Cl$. A single product was formed ($^{31}P\text{-}\{^1H\}$ NMR evidence) and isolated as a yellow solid. This showed in its IR spectrum a very intense band at 2088 cm^{-1}, typical for a C≡O co-ordinated to rhodium(III), in addition there was a strong band at 1935 cm^{-1} due to ν(C=C=C).[10] The $^{13}C\text{-}\{^1H\}$ NMR spectrum of **4** also supported the allenic structure and the central allenic carbon (C=*C*=C) gave a singlet at δ 204.8.[10,27]

Table 1 Infrared[a] and $^{31}P\text{-}\{^1H\}$ NMR[b] data

Compound	ν(C≡O)	δ_P	$^1J(RhP)$/Hz
I[c]	—	−22.4	—
1	1974s	52.3	165
2	2097s	45.2	101
3	2060s	54.0	121
4[d]	2088s	51.7	118
5	—	53.3	125
6[e]	2084s	85.5	112
7[f]	2070s	98.8	66

[a] As KBr disc, in cm^{-1}, s = strong. [b] Recorded at 36.2 MHz in $CDCl_3$, unless otherwise indicated; chemical shifts (δ) are in ppm relative to 85% H_3PO_4. [c] ν(N−H) 3165w and ν(C=O) 1665s cm^{-1}. [d] ν(C=C=C) 1935m cm^{-1}. [e] ν(C=O) 1720s cm^{-1}. [f] ν(C=O) 1700s cm^{-1}.

Treatment of complex **1** with allyl bromide gave a single product which showed no band in the IR spectrum corresponding to ν(C≡O) and in the $^{13}C\text{-}\{^1H\}$ NMR spectrum there was no resonance corresponding to C≡O. We observed a similar decarbonylation reaction when we treated allyl chloride with $[Rh(CO)\{PPh_2CH_2C(Bu^t){=}N{-}N{=}CH[C_6H_2O(OMe)_2]\}]$.[10] We formulate this complex as an η^3-allylrhodium(III) adduct of stereochemistry **5**. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **5** showed a doublet at δ 53.3 with $^1J(RhP) = 125$ Hz. In the ^1H NMR spectrum, the terminal *anti* protons of the η^3-allyl group each gave a doublet, one at δ 2.16 [$^3J(HH) = 10.0$ Hz] and the other at δ 3.85 [$^3J(HH) = 12.2$ Hz]; the large value of $^3J(HH)$ is typical for *trans*-vicinal coupling. The *syn*-protons gave multiplets, at δ 2.35 and 4.49. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum the methylene carbon (CH_2P) gave a doublet resonance at δ 48.0 with $^1J(PC) = 36.8$ Hz. The resonances at δ 53.5, 63.3 and 98.3 were assigned to the two $=CH_2$ carbons and the =CH carbon of the η^3-allyl group.[28]

Dimethyl acetylenedicarboxylate, $MeO_2CC{\equiv}CCO_2Me$ (dmad), is an electronegative acetylene and often forms adducts with metals which are in a low valency state. Sometimes such an interaction is followed by carbon–carbon bond formation giving, for example, a metallacyclopentadiene, sometimes carbon–carbon bond formation continues and hexa(methoxycarbonyl)benzene is formed catalytically, *e.g.* by treatment of *trans*-$[RhCl(CO)(PPh_3)_2]$ with dmad.[29]

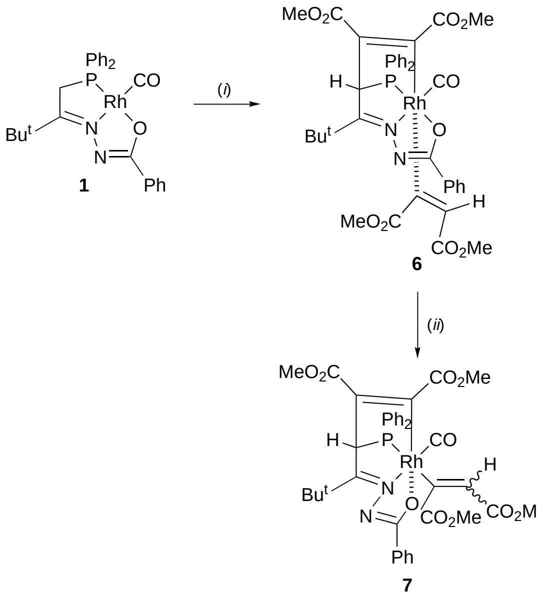
We treated the carbonylrhodium(I) complex **1** with an excess of dmad at 20 °C in dichloromethane solution and followed the progress of the reaction by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. We found conversion of **1** to give a single new product, characterised by a doublet at δ 85.5 $^1J(RhP) = 112$ Hz. After 2 h **1**, characterised by the doublet at δ 52.3 $^1J(RhP) = 165$ Hz, had essentially all reacted to give the new product which was isolated as pale yellow crystals. Elemental analysis and the mass spectrum (*m*/*z* 816, M^+) of this product showed that **1** had taken up 2 mol of dmad. The crystal structure of this product was determined and is shown in Fig. 1 and diagrammatically as **6** in Scheme 2. It shows that one acetylenic carbon of dmad has attacked the CH_2 carbon of the terdentate (*P*,*N*,*O*) ligand in **1** and the other acetylenic carbon is bonded to rhodium to give a tetradentate (*P*,*N*,*O*,*C*) ligand with three fused five-membered chelate rings. The second dmad has become bonded to rhodium as a $C(CO_2Me){=}CH(CO_2Me)$ moiety in which the Rh and hydrogen are mutually *cis* around the C=C bond. The crystal structure also showed that in the *P*,*N*,*O* part the P and O are co-ordinated in mutually *trans* positions, as they were in **1**.

The infrared spectrum of complex **6** showed a strong band at 1720 cm^{-1} due to the ν(C=O) and a strong band at 2084 cm^{-1} due to ν(C≡O). The ^1H NMR spectrum showed four singlets of

Table 2 Proton NMR data[a]

	$\delta(Bu^t)$	$\delta(CH_2P)/\delta(CHP)$	Others
I[b]	1.50 (9 H, s)	3.17 (2 H, s)	9.57 (1 H, br, NH)[c]
1[b]	1.50 (9 H, s)	3.99 [2 H, d, ^2J(PH) 10.7]	
2	1.61 (9 H, s)	4.43 [2 H, d, ^2J(PH) 12.6]	
3	1.62 (9 H, s)	4.31 [1 H, dd, ^2J(HH) 12.5, ^2J(PH) 13.3] 4.34 [1 H, dd, ^2J(HH) 12.5, ^2J(PH) 11.4]	0.86 [3 H, t, ^3J(PH) 2.2, ^2J(RhH) 2.2, RhMe]
4	1.62 (9 H, s)	4.34 [1 H, dd, ^2J(PH) 13.2, ^2J(HH) 18.5] 4.36 [1 H, dd, ^2J(PH) 11.9, ^2J(HH) 18.5]	3.62 [1 H, ddd, ^2J(HH) 7.8, ^4J(HH) 6.0, ^4J(RhH) 1.3, $=CH_2$], 4.03 [1 H, ddd, ^2J(HH) 7.8, ^4J(HH) 6.0, ^4J(RhH) 1.3, $=CH_2$], 4.95 [1 H, m, ^4J(HH) 6.0, ^2J(RhH) 4.3, ^3J(PH) 2.5, RhCH]
5	1.66 (9 H, s)	4.08 [1 H, dd, ^2J(PH) 13.9, ^2J(HH) 18.1] 4.25 [1 H, dd, ^2J(PH) 10.2, ^2J(HH) 18.1]	2.16 [1 H, d, ^3J(HH) 10.0, H_{anti}], 2.35 (1 H, m, H_{syn}), 3.85 [1 H, d, ^3J(HH) 12.2, H_{anti}], 4.49 (1 H, m, H_{syn}), 4.51 (1 H, m, CHRh)
6	1.62 (9 H, s)	5.58 [1 H, d, ^2J(PH) 12.8, CHP]	3.38 (3 H, s, OMe), 3.59 (3 H, s, OMe), 3.68 (3 H, s, OMe), 3.75 (3 H, s, OMe), 4.99 [1 H, d, ^3J(RhH) 1.0, C=CH]
7	1.15 (9 H, s)	5.50 [1 H, d, ^2J(PH) 11.5, CHP]	3.55 (3 H, s, OMe), 3.69 (3 H, s, OMe), 3.74 (3 H, s, OMe), 3.79 (3 H, s, OMe), 5.45 [1 H, dd, ^3J(RhH) 2.0, ^4J(PH) 12.5, C=CH]

[a] Recorded at 250 MHz, chemical shifts δ relative to $SiMe_4$, solvent $CDCl_3$ unless stated; coupling constants *J* in Hz; s = singlet, d = doublet, br = broad, m = multiplet, ddd = double doublet of doublets and t = triplet; phenyl protons were observed between δ 7.03 and 7.89. [b] Recorded at 100 MHz. [c] D_2O exchange.



Scheme 2 (*i*) $MeO_2CC{\equiv}CCO_2Me$; (*ii*) heat

equal intensity at δ 3.38, 3.59, 3.68 and 3.75 for the four OMe groups. The methine proton (CHP) resonated at δ 5.58 as a doublet with ^2J(PH) = 12.8 Hz, and the resonance of the alkenyl proton appeared at δ 4.99 with coupling to rhodium [^3J(RhH) = 1.0 Hz]; the coupling to phosphorus was too small to be resolved. The ^{13}C-{^1H} NMR spectrum was recorded and the carbon resonances were assigned with the aid of an attached proton test (APT) and by two-dimensional ^1H–^{13}C-{^1H} COSY (correlation spectroscopy) experiments. The resonance of the C≡O carbon was a doublet of doublets at δ 186.8 [^2J(PC) = 12.3 and ^1J(RhC) = 58.2 Hz], whilst the two singlets at δ 171.2 and 177.7 were assigned as resonances of the two RhC=C*C*O_2Me carbons. The resonances of the two RhC*C*O_2Me carbons were doublets at δ 174.5 and 175.6. The doublet of doublets at δ 170.9 with ^2J(PC) = 3.1 Hz and ^1J(RhC) = 23.3 Hz and a doublet at δ 187.9 with ^1J(RhC) = 20.0 Hz were assigned to the two Rh*C*=C carbons. The smaller ^2J(PC) values (3.1 and 0 Hz) indicate that the carbon atoms are *cis* to the phosphorus atom.

When we heated complex **6** in benzene solution at 78 °C for 55 h the ^{31}P-{^1H} NMR spectrum indicated its complete conversion into a new compound which resonated at δ 98.8 with ^1J(RhP) = 66 Hz. This new species was readily isolated as a yellow solid. The microanalytical and mass spectral data for this new complex (see Experimental section) established that it was isomeric with **6**. We tentatively formulate it as the structure **7** on the basis of the following spectroscopic data. The infrared spectrum showed the ν(C=O) at 1700 cm^{-1} whilst the high value of ν(C≡O) at 2070 cm^{-1} indicates the +3 oxidation state for rhodium.[24] The ^1H and ^{13}C-{^1H} NMR data are similar to those of **6**. The methyl protons of the CO_2*Me* groups gave four singlets at δ 3.55, 3.69, 3.74 and 3.79. The CHP proton gave a doublet at δ 5.50 with ^2J(PH) = 11.5 Hz. The resonance of the alkenyl proton was a doublet of doublets at δ 5.45 with a sizable five-bond coupling of 12.5 Hz to phosphorus and ^3J(RhH) = 2 Hz, suggesting that the alkenyl group was probably *trans* to the phosphorus atom since for complex **6** the five-bond coupling to phosphorus was too small to be resolved. In the ^{13}C-{^1H} NMR spectrum of **7** the resonance of the RhC≡O carbon was a doublet of doublets at δ 185.2 [^2J(PC) = 7.6 and ^1J(RhC) = 61.0 Hz]; the small value ^2J(PC≡O) of 7.6 Hz indicates that the carbonyl ligand is *cis* to P. The resonance at δ 164.9 with ^2J(PC) = 125.9 and ^1J(RhC) = 27.8 Hz was assigned to the Rh*C*=$CHCO_2Me$ carbon. Such a large ^2J(PC) value of 125.9 Hz is expected for a carbon *trans* to a phosphorus atom; similar values have been found for some transition-metal complexes, *e.g.* $^2J(P\text{–}M\text{–}C_{trans}) \approx 75\text{–}130$ Hz where M = Pt, Ir or Ru.[6,9,30]

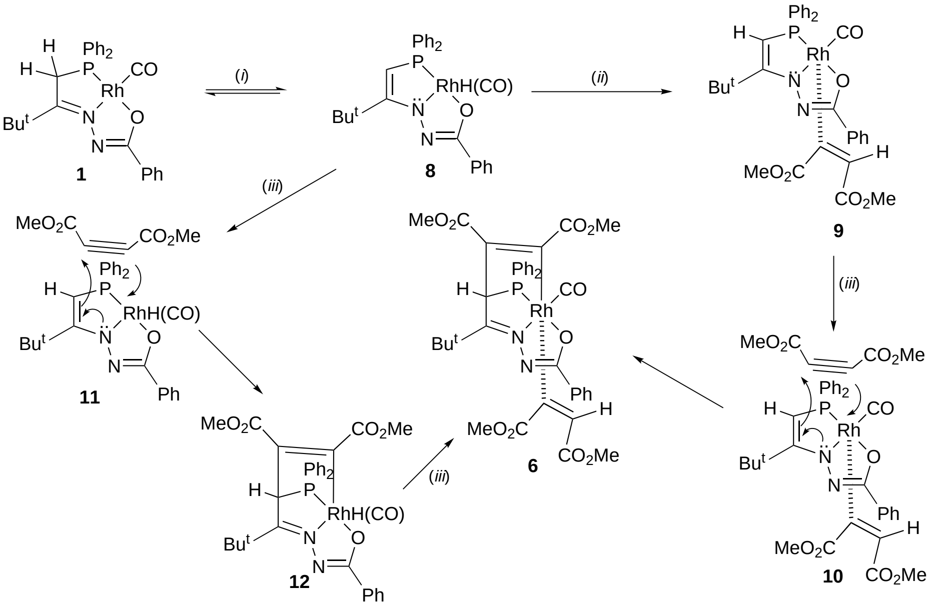
We suggest two possible sequences of steps for the conversion of complex **1** into **6** (see Scheme 3). We have shown previously with iridium chemistry of the azine diphosphine *Z*,*Z*-$PPh_2CH_2C(Bu^t)$=N–N=$C(Bu^t)CH_2PPh_2$ that reversible migration of a methylene hydrogen to iridium to give an iridium(III) hydride could occur rapidly, possibly *via* PPh_2CH=$C(Bu^t)$-NH–N=$C(Bu^t)CH_2PPh_2$ and oxidative addition of N–H to iridium(I).[31,32] We suggest a similar process is involved in the conversion of **1** into the (ene–hydrazone)rhodium hydride **8**. Co-ordination of dmad to **8** followed by *cis* migration of hydride to the β-carbon of the co-ordinated dmad then gives **9**. Michael-type attack on the second mol of dmad by the ene–hydrazone carbon followed by attack of the second dmad carbon on rhodium (see **10**) then gives **6**. Alternatively, Michael-type attack on dmad by **8** might occur first to give **11** and then **12**; **12** is then attacked by a second mol of dmad with hydride migration to give **6**.

We tentatively suggest that in the conversion of complex **6** into **7** a Rh–O bond breaks to give a five-co-ordinated intermediate which rearranges and when the Rh–O bond reforms isomer **7** is preferred.

The crystal structure of the rhodium(III) complex **6** was determined and is shown in Fig. 1. Important features are: (*i*) an acetylenic carbon of a dmad has attacked the carbon of the activated CH_2, the other acetylenic carbon becoming directly bonded to rhodium; thus the original *P*,*N*,*O* terdentate ligand is transformed into a *P*,*N*,*O*,*C* tetradentate ligand; (*ii*) the

Table 3 Selected interatomic distances (Å) and angles (°) with e.s.d.s in parentheses

Rh−C(13)	1.942(8)	Rh−N(4)	2.054(5)	C(9)−O(9)	1.211(8)	C(9)−O(10)	1.348(8)
Rh−O(6)	2.108(4)	Rh−C(8)	2.116(6)	O(10)−C(10)	1.484(8)	C(11)−O(11)	1.224(9)
Rh−C(14)	2.128(6)	Rh−P	2.299(2)	C(11)−O(12)	1.348(9)	O(12)−C(12)	1.457(9)
P−C(111)	1.826(7)	P−C(121)	1.829(6)	C(13)−O(13)	1.144(8)	C(14)−C(17)	1.359(9)
P−C(2)	1.871(7)	C(2)−C(3)	1.513(9)	C(14)−C(15)	1.517(9)	C(15)−O(15)	1.197(8)
C(2)−C(7)	1.571(8)	C(3)−N(4)	1.331(8)	C(15)−O(16)	1.349(8)	O(16)−C(16)	1.500(9)
N(4)−N(5)	1.399(7)	N(5)−C(6)	1.372(8)	C(17)−C(18)	1.476(9)	C(18)−O(18)	1.211(9)
C(6)−O(6)	1.316(7)	C(7)−C(8)	1.387(9)	C(18)−O(19)	1.389(8)	O(19)−C(19)	1.447(9)
C(7)−C(11)	1.487(9)	C(8)−C(9)	1.509(9)				
C(13)−Rh−N(4)	176.6(3)	C(13)−Rh−O(6)	101.4(2)	O(6)−Rh−C(14)	83.6(2)	C(8)−Rh−C(14)	170.9(2)
N(4)−Rh−O(6)	79.6(2)	C(13)−Rh−C(8)	95.4(3)	C(13)−Rh−P	97.3(2)	N(4)−Rh−P	81.7(2)
N(4)−Rh−C(8)	81.3(2)	O(6)−Rh−C(8)	97.6(2)	O(6)−Rh−P	161.19(12)	C(8)−Rh−P	78.6(2)
C(13)−Rh−C(14)	93.2(3)	N(4)−Rh−C(14)	90.1(2)	C(14)−Rh−P	97.4(2)		
C(3)−C(2)−C(7)	107.4(5)	C(3)−C(2)−P	108.6(4)	O(10)−C(9)−C(8)	111.8(6)	C(9)−O(10)−C(10)	115.5(6)
C(7)−C(2)−P	98.0(4)	N(4)−C(3)−C(2)	110.1(5)	O(11)−C(11)−O(12)	124.6(7)	O(11)−C(11)−C(7)	124.7(7)
C(3)−N(4)−N(5)	122.9(5)	C(3)−N(4)−Rh	122.7(4)	O(12)−C(11)−C(7)	110.7(7)	C(11)−O(12)−C(12)	115.2(7)
N(5)−N(4)−Rh	114.1(4)	C(6)−N(5)−N(4)	109.4(5)	O(13)−C(13)−Rh	175.9(6)	C(17)−C(14)−C(15)	122.6(6)
O(6)−C(6)−N(5)	128.1(6)	O(6)−C(6)−C(61)	113.6(5)	C(17)−C(14)−Rh	122.0(5)	C(15)−C(14)−Rh	115.4(4)
N(5)−C(6)−C(61)	118.3(5)	C(6)−O(6)−Rh	106.0(4)	O(15)−C(15)−O(16)	123.1(7)	O(15)−C(15)−C(14)	123.5(7)
C(8)−C(7)−C(11)	126.7(6)	C(8)−C(7)−C(2)	117.4(5)	O(16)−C(15)−C(14)	113.3(6)	C(15)−O(16)−C(16)	117.4(6)
C(11)−C(7)−C(2)	115.9(6)	C(7)−C(8)−C(9)	127.1(6)	C(14)−C(17)−C(18)	124.1(6)	O(18)−C(18)−O(19)	125.1(6)
C(7)−C(8)−Rh	113.1(4)	C(9)−C(8)−Rh	119.6(5)	O(18)−C(18)−C(17)	125.8(7)	O(19)−C(18)−C(17)	109.0(6)
O(9)−C(9)−O(10)	122.2(6)	O(9)−C(9)−C(8)	125.8(6)	C(18)−O(19)−C(19)	116.5(6)		



Scheme 3 Possible mechanism(s) for the conversion of complex **1** into **6**. (*i*) 1,3-Proton shift and N−H addition; (*ii*) dmad co-ordination and hydrogen migration; (*iii*) dmad

second dmda has interacted with Rh−H to give an *E*-RhC-(CO_2Me)=CH(CO_2Me) moiety, *i.e.* effectively Rh−H has added *cis* to the −C≡C−; (*iii*) the C≡O ligand remains *trans* to nitrogen as it was in the starting square-planar rhodium(I) complex **1**. Selected bond distances and angles are given in Table 3 whilst crystal data and details of refinement are given in Table 4. The bond lengths Rh−P [2.299(2)], Rh−N(4) [2.054(5)] and Rh−O(6) [2.108(4)] are similar to such bond lengths previously reported for rhodium(III) complexes.[28,33–36] The bond angles N(4)−Rh−O(6) [79.6(2)], N(4)−Rh−C(8) [81.3(2)] and N(4)−Rh(1)−P [81.7(2)°] are all considerably less than 90° because of restrictions imposed by the tetradentate ligand.

Experimental

All the reactions were carried out in an inert atmosphere of dry nitrogen. The NMR spectra were recorded using a JEOL FX-90Q (operating frequencies for ^1H and ^{31}P, 89.5 and 36.2 MHz, respectively), a JEOL FX-100 (operating frequencies for ^1H and ^{31}P, 99.5 and 40.25 MHz), a Bruker ARX-250 (operating frequencies for ^1H and ^{13}C, 250.13 and 62.9 MHz) or a Bruker AM-400 spectrometer (operating frequencies for ^1H, ^{31}P and ^{13}C, 400.13, 161.9 and 100.6 MHz). The ^1H and ^{13}C chemical shifts are relative to tetramethylsilane and ^{31}P shifts to 85% phosphoric acid. Infrared spectra were recorded using a Perkin-Elmer model 257 grating spectrometer (4000–600 cm^{-1}) or a Philips Scientific SP2000 (4000–200 cm^{-1}) spectrometer, fast atom bombardment (FAB) mass spectra using a VG Autospec spectrometer with 8 kV acceleration.

The phosphine *Z*-$PPh_2CH_2C(Bu^t)=NNMe_2$ was prepared as reported.[2]

Preparations

***Z*-$PPh_2CH_2C(Bu^t)=NNHC(=O)Ph$ I.** A solution of the phosphino-*N*,*N*-dimethylhydrazone *Z*-$PPh_2CH_2C(Bu^t)=NNMe_2$ (6.07 g, 18.6 mmol), benzohydrazide (9.03 g, 66.0 mmol) and acetic acid (10 cm^3) in ethanol (90 cm^3) was heated under reflux for 12 h. Water (25 cm^3) was then added to the mixture to give

Table 4 Crystal data and details of refinement for compound **6**

Empirical formula	$C_{38}H_{38}N_2O_{10}PRh{\cdot}0.5C_6H_6$
M	855.64[a]
T/K	200
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	9.624(2)
b/Å	14.720(3)
c/Å	16.265(3)
α/°	105.917(10)
β/°	92.517(10)
γ/°	103.004(12)
U/Å^3	2145.3(7)
Z	2
D_c/Mg m^{-3}	1.325
μ/mm^{-1}	0.491
F(000)	882
Absorption correction	Empirical *via* ψ scans
Maximum, minimum transmission factors	0.833, 0.730
Crystal size/mm	0.15 × 0.12 × 0.08
θ_{min}, θ_{max}/°	3.62, 66.39
hkl Ranges	−11, 10; −17, 16; 0, 19
Independent reflections, p	7280
Reflections with $F_o^2 > 2\sigma F_o^2$	3860
Weighting scheme parameter a[b]	0.0600
Data, restraints, parameters (n)	7280, 60, 489
Goodness of fit on F^2, S[c]	1.002
$R1$[d]	0.050
$wR2$[e]	0.142
Largest difference map peak and hole/e Å^{-3}	0.841, −1.036

[a] Includes solvate molecule. [b] $w = [\sigma^2(F_o)^2 + aP^2]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$ overall scale factor. [c] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$. [d] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [e] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{\frac{1}{2}}$.

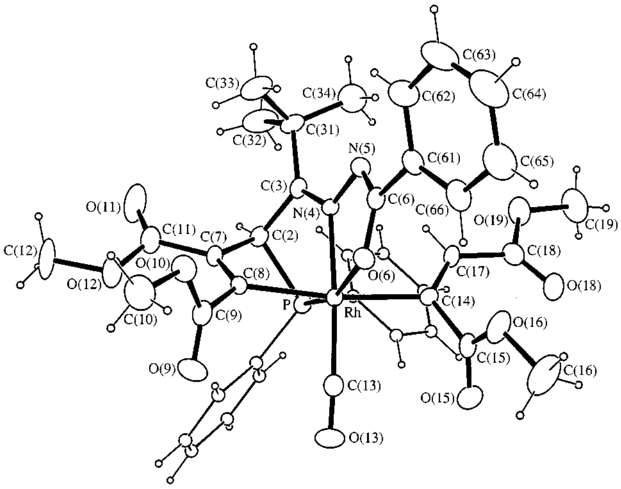


Fig. 1 Crystal structure of the bis(dimethylacetylenedicarboxylate) adduct **6**

the required phosphine **I** as a white solid. Yield 4.90 g, 65% (Found: C, 74.4; H, 6.6; N, 6.9. $C_{25}H_{27}N_2OP$ requires C, 74.6; H, 6.8; N, 6.95%). *m/z* (electron impact, EI) 400 (M − 2). ^{13}C-{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 27.6 [1 C, d, ^1J(PC) 48.3 Hz, CH$_2$P], 28.3 (3 C, s, C*Me*$_3$), 39.4 (1 C, s, *C*Me$_3$), 162.4 (1 C, s, C=N) and 168.2 (1 C, s, C=O).

[Rh(CO){PPh$_2$CH$_2$C(Bu^t)=N–N=C(Ph)O}] 1. A solution containing the phosphine **I** (481 mg, 1.19 mmol) and [{RhCl(CO)$_2$}$_2$] (233 mg, 0.59 mmol) in dichloromethane (5 cm^3) was put aside for 3 h. The solvent was then evaporated to low volume under reduced pressure and methanol added to the residue to give complex **1** as a yellow solid. Yield 263 mg, 41% (Found: C, 57.45; H, 4.9; N, 5.0. $C_{26}H_{26}N_2O_2PRh{\cdot}0.2CH_2Cl_2$ requires C, 57.3; H, 4.8; N, 5.1%). *m/z* (FAB, for ^{103}Rh) 533 (M + 1) and 505 (M + 1 − CO). ^{13}C-{^{1}H} NMR (62.9 MHz, CDCl$_3$): δ 28.7 (3 C, s, C*Me*$_3$), 38.8 [1 C, d, ^3J(PC) 9.9, *C*Me$_3$], 47.9 [1 C, d, ^1J(PC) 29.9, CH$_2$P], 176.0 [1 C, dd, J(PC) or J(RhC) 1.8 or 5.6, C=N], 176.6 [1 C, d, J(PC) or J(RhC) 1.8, C=N] and 191.7 [1 C, dd, ^2J(PC) 19.1, ^1J(RhC) 72.2 Hz, C≡O].

[RhBr$_2$(CO){PPh$_2$CH$_2$C(Bu^t)=N–N=C(Ph)O}] 2. A solution containing complex **1** (692 mg, 0.13 mmol) in dichloromethane (5 cm^3) was treated with an excess of bromine solution in carbon tetrachloride (0.32 cm^3, 0.751 mol dm^{-3}, 0.24 mmol) and was put aside for 1 h. The solvent was then evaporated to low volume under reduced pressure and methanol added to the residue to give **2** as an orange solid. Yield 51 mg, 57% (Found: C, 43.35; H, 3.75; N, 3.75. $C_{26}H_{26}Br_2N_2O_2PRh{\cdot}0.5CH_2Cl_2$ requires C, 43.35; H, 3.7; N, 3.8%). *m/z* (FAB, for ^{103}Rh and ^{79}Br) 693 (M + 3), 665 (M + 3 − CO) and 583 (M − CO − Br).

[RhMe(I)(CO){PPh$_2$CH$_2$C(Bu^t)=N–N=C(Ph)O}] 3. A solution containing complex **1** (73 mg, 0.13 mmol) in dichloromethane (5 cm^3) was treated with an excess of methyl iodide (0.3 cm^3) and was put aside for 3 h. The solvent was then evaporated to low volume under reduced pressure and methanol added to the residue to give **3** as a reddish brown solid. Yield 69 mg, 75% (Found: C, 47.9; H, 4.3; I, 18.9; N, 4.2. $C_{27}H_{30}IN_2O_2PRh$ requires C, 48.0; H, 4.5; I, 18.8; N, 4.15%). *m/z* (FAB, for ^{103}Rh) 675 (M^+) and 547 (M − HI). ^{13}C-{^{1}H} NMR (62.9 MHz, CDCl$_3$): δ 16.7 [1 C, dd, ^2J(PC) 2.8, ^1J(RhC) 19.9, RhMe], 28.9 (3 C, s, C*Me*$_3$), 38.9 [1 C, d, ^3J(PC) 10.5, *C*Me$_3$], 47.0 [1 C, d, ^1J(PC) 35.5, CH$_2$P], 170.3 (1 C, s, C=N), 176.3 [1 C, d, J(PC) or J(RhC) 2.1, C=N] and 187.0 [1 C, dd, ^2J(PC) 13.8, ^1J(RhC) 58.4 Hz, C≡O].

[RhCl(CH=C=CH$_2$)(CO){PPh$_2$CH$_2$C(Bu^t)=N–N=C(Ph)O}] 4. A solution containing complex **1** (73 mg, 0.14 mmol) in dichloromethane (5 cm^3) was treated with an excess of propargyl chloride (0.3 cm^3) and put aside for 24 h. The solvent was then evaporated to low volume under reduced pressure and methanol added to the residue to give **4** as a yellow solid. Yield 44 mg, 52% (Found: C, 56.4; H, 4.7; N, 4.5. $C_{29}H_{29}ClN_2O_2PRh{\cdot}0.2CH_2Cl_2$ requires C, 56.2; H, 4.75; N, 4.5%). *m/z* (FAB, for ^{103}Rh and ^{35}Cl) 542 (M − CO − HCl). ^{13}C-{^{1}H} NMR (62.9 MHz, CDCl$_3$): δ 28.7 (3 C, s, C*Me*$_3$), 39.1 [1 C, d, ^3J(PC) 9.7, *C*Me$_3$], 45.9 [1 C, d, ^1J(PC) 33.9, CH$_2$P], 72.1 (1 C, s, =CH$_2$), 81.5 [1 C, dd, ^1J(RhC) 28.0, ^2J(PC) 6.0, RhCH], 170.0 (1 C, s, C=N), 176.0 (1 C, s, C=N), 184.1 [1 C, dd, ^2J(PC) 13.8, ^1J(RhC) 58.0 Hz, C≡O] and 204.8 (1 C, s, C=*C*=C).

[RhBr(η^3-C$_3$H$_5$){PPh$_2$CH$_2$C(Bu^t)=N–N=C(Ph)O}] 5. A solution containing complex **1** (66 mg, 0.12 mmol) in dichloromethane (5 cm^3) was treated with an excess of allyl bromide (0.3 cm^3) and put aside for 0.5 h. The solvent was then evaporated to low volume under reduced pressure and methanol added to the residue to give **5** as a yellow solid. Yield 59 mg, 73% (Found: C, 52.05; H, 4.75; N, 4.1. $C_{28}H_{31}BrN_2OPRh{\cdot}0.25CH_2Cl_2$ requires C, 52.35; H, 4.95; N, 4.35%). *m/z* (FAB, for ^{103}Rh and ^{79}Br) 545 (M − Br). ^{13}C-{^{1}H} NMR (62.9 MHz, CDCl$_3$): δ 28.9 (3 C, s, C*Me*$_3$), 39.2 [1 C, d, ^3J(PC) 9.7, *C*Me$_3$], 48.0 [1 C, d, ^1J(PC) 36.8, CH$_2$P], 53.5 [1 C, d, ^1J(RhC) 13.1, RhCH$_2$], 63.3 [1 C, d, ^1J(RhC) 7.1, RhCH$_2$], 98.3 [1 C, d, ^1J(RhC) 4.7, RhCH], 171.0 (1 C, s, C=N) and 174.9 [1 C, d, J(PC) 3.7 Hz, C=N].

[Rh(CO){C(CO$_2$Me)=CHCO$_2$Me}{PPh$_2$CH[C(CO$_2$Me)=C-(CO$_2$Me)]C(Bu^t)=N–N=C(Ph)O}] 6. A solution containing complex **1** (46 mg, 0.02 mmol) in dichloromethane (5 cm^3) was treated with an excess of dimethyl acetylenedicarboxylate (0.018 cm^3, 0.15 mmol) and put aside for 2 h. The solvent was then evaporated to low volume under reduced pressure and methanol added to the residue to give **6** as a yellow solid. Yield 59 mg, 73% (Found: C, 53.95; H, 4.6; N, 3.25. $C_{38}H_{38}N_2O_{10}$-

PRh·0.5CH$_2$Cl$_2$ requires C, 53.85; H, 4.6; N, 3.25%). *m*/*z* (FAB, for ^{103}Rh) 816 (M^+). ^{13}C-{^{1}H} NMR (62.9 MHz, CDCl$_3$): δ 29.6 (3 C, s, C*Me*$_3$), 39.2 [1 C, d, ^3J(PC) 8.1, *C*Me$_3$], 50.1 (1 C, s, OMe), 50.2 (1 C, s, OMe), 51.8 (1 C, s, OMe), 52.4 (1 C, s, OMe), 63.1 [1 C, dd, ^1J(PC) 32.4, ^2J(RhC) 2.1, CHP], 123.4 [1 C, d, *J*(PC) or *J*(RhC) 6.1, H*C*=CRh], 128.4 (1 C, s, *C*=CRh), 161.2 [1 C, dd, *J*(PC) or *J*(RhC) 8.8 or 1.2, C=N], 163.5 [1 C, d, *J*(PC) or *J*(RhC) 1.6, C=N], 170.9 [1 C, dd, ^1J(RhC) 23.3, ^2J(PC) 3.1, Rh*C*=C], 171.2 (1 C, s, RhC=C*C*O$_2$Me), 174.5 [1 C, d, *J*(PC) or *J*(RhC) 1.6, RhC*C*OMe], 175.6 [1 C, d, *J*(PC) or *J*(RhC) 1.6, RhC*C*O$_2$Me], 177.7 (1 C, s, RhC=C*C*O$_2$Me), 186.8 [C, dd, ^2J(PC) 12.3, ^1J(RhC) 58.2, C≡O] and 187.9 [1 C, d, ^1J(RhC) 20.0 Hz, Rh*C*=C].

[Rh(CO){C(CO$_2$Me)=CHCO$_2$Me}{PPh$_2$CH[C(CO$_2$Me)=C-(CO$_2$Me)]C(Bu^t)=N−N=C(Ph)O}] 7. A solution containing complex **6** (189 mg, 0.23 mmol) in benzene (5 cm^3) was heated at 78 °C for 3 d. The solvent was then evaporated to low volume under reduced pressure and methanol added to the residue to give **7** as a yellow solid. Yield 154 mg, 82% (Found: C, 56.05; H, 4.6; N, 2.9. C$_{38}$H$_{38}$N$_2$O$_{10}$PRh requires C, 55.9; H, 4.7, N, 3.45%). *m*/*z* (FAB, for ^{103}Rh) 816 (M^+). ^{13}C-{^{1}H} NMR (62.9 MHz, CDCl$_3$): δ 27.6 (3 C, s, C*Me*$_3$), 38.7 [1 C, d, ^3J(PC) 2.5, *C*Me$_3$], 51.1 (1 C, s, OMe), 51.3 (1 C, s, OMe), 51.9 (1 C, s, OMe), 52.6 (1 C, s, OMe), 61.4 [1 C, dd, ^1J(PC) 33.2, ^2J(RhC) 2.9, CHP], 125.4 [1 C, d, *J*(PC) or *J*(RhC) 1.7, H*C*=CRh], 128.8 (1 C, s, *C*=CRh), 161.6 [1 C, dd, *J*(PC) or *J*(RhC) 8.8 or 1.2, C=N], 163.7 [1 C, dd, *J*(PC) or *J*(RhC) 2.7 or 15.3, C=N], 164.9 [1 C, dd, ^1J(RhC) 27.8, ^2J(PC) 125.9, Rh*C*=C], 171.9 (1 C, s, RhC=C*C*O$_2$Me), 172.0 [1 C, d, *J*(PC) or *J*(RhC) 6.5, RhC*C*O$_2$Me], 172.4 [1 C, d, ^1J(RhC) 24.5, Rh*C*=C], 174.1 (1 C, s, RhC=C*C*O$_2$Me), 175.0 [1 C, d, *J*(PC) or *J*(RhC) 5.4, RhC*C*O$_2$Me] and 185.2 [1 C, dd, ^2J(PC) 7.6, ^1J(RhC) 61.0 Hz, C≡O].

Crystallography

Crystallisation of complex **6** from C$_6$H$_6$–EtOH gave a suitable crystal as a benzene solvate. All crystallographic measurements were made on a Stoe STADI4 diffractometer operating in the ω–θ scan mode using graphite-monochromated Cu-Kα radiation ($\lambda = 1.541\,84$ Å). Crystal data are given in Table 4 together with refinement details. Cell dimensions were refined from the values of 40 selected reflections (together with their Freidel opposites) measured at ±2θ in order to minimise systematic errors.

The structure was solved by heavy-atom methods using SHELXS 86[37] and developed by full-matrix least-squares refinement (on F^2) using SHELXL 93.[38] The unit cell also contains a benzene solvate molecule which is positioned across the inversion centre at ($1.0 - x$, y, $1.0 - z$). All non-hydrogen atoms were refined with anisotropic displacement parameters, including those of the solvate molecule. Restraints were applied to the phenyl rings so that they remained flat with overall C_{2v} symmetry. All hydrogen atoms were constrained to idealised positions with a riding model including free rotation of methyl groups. Selected bond lengths and angles are in Table 3.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/548.

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References

1 G. R. Newkome and D. L. Fishel, *J. Org. Chem.*, 1966, **31**, 677.
2 K. K. Hii, S. D. Perera, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1992, 2361 and refs. therein.
3 K. K. Hii, S. D. Perera, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1994, 103 and refs. therein.
4 S. D. Perera and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1995, 633 and refs. therein.
5 S. D. Perera and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1994, 1201; *J. Chem. Soc., Dalton Trans.*, 1995, 3861.
6 S. D. Perera and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1994, 1203; S. D. Perera, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1995, 1689.
7 S. D. Perera and B. L. Shaw, *Inorg. Chim. Acta*, 1995, **228**, 127.
8 S. D. Perera and B. L. Shaw, *J. Organomet. Chem.*, 1994, **479**, 117.
9 S. D. Perera and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1995, 641.
10 K. K. Hii, S. D. Perera and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1994, 3589.
11 K. K. Hii, S. D. Perera and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1995, 625.
12 S. D. Perera, M. Shamsuddin and B. L. Shaw, *Can. J. Chem.*, 1995, **73**, 1010.
13 P. Domiano, A. Musatti, M. Nardelli, C. Pelizzi and G. Predieri, *J. Chem. Soc., Dalton Trans.*, 1979, 1266 and refs. therein.
14 A. Bonardi, C. Merlo, C. Pelizzi, G. Pelizzi, P. Tarasconi and F. Cavatorta, *J. Chem. Soc., Dalton Trans.*, 1991, 1063 and refs. therein.
15 L. Labib, T. E. Khalil, M. F. Iskander and L. S. Refaat, *Polyhedron*, 1996, **15**, 3697 and refs. therein.
16 J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 211.
17 A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1969, 597 and refs. therein.
18 G. C. Cristoph, P. Blum, W. C. Liu, A. Elia and D. W. Meek, *Inorg. Chem.*, 1979, **18**, 894.
19 E. M. Hyde, J. D. Kennedy, B. L. Shaw and W. MacFarlane, *J. Chem. Soc., Dalton Trans.*, 1977, 1591.
20 U. U. Ike, S. D. Perera, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1995, 2057.
21 S. D. Perera, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1992, 1469.
22 S. D. Perera, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1991, 1183.
23 J. P. Collman and L. S. Hegedus, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CF, 1980, p. 210; A. G. Constable, C. R. Langrick, B. Shabanzadeh and B. L. Shaw, *Inorg. Chim. Acta*, 1982, **65**, L151.
24 J. Chatt and B. L. Shaw, *J. Chem. Soc. A*, 1966, 1437; R. F. Heck, *J. Am. Chem. Soc.*, 1964, **86**, 2796; M. C. Baird, J. T. Mague, J. A. Osborn and G. Wilkinson, *J. Chem. Soc. A*, 1967, 1347.
25 J. P. Collman, J. N. Cawse and J. W. Kang, *Inorg. Chem.*, 1969, **8**, 2574.
26 M. D. Johnson and C. Mayle, *Chem. Commun.*, 1969, 192.
27 P. Sohar, *NMR Spectroscopy*, CRC Press, Boca Raton, FL, 1983, vol. 2, p. 179.
28 K. Ossalaka, J.-C. Choi, T. Koizumi, I. Yamaguchi and T. Yamamoto, *Organometallics*, 1995, **14**, 4962.
29 J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, 1967, **89**, 844.
30 J. D. Vessey and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1993, 51.
31 S. D. Perera and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1995, 865.
32 S. D. Perera, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1996, 3111.
33 M. Cano, J. V. Heras, M. A. Lobo, E. Pinilla and M. A. Monge, *Polyhedron*, 1992, **11**, 2679.
34 M. Cano, J. V. Heras, M. A. Lobo, M. Martinez, E. Pinilla and M. A. Monge, *Polyhedron*, 1991, **10**, 187.
35 M. Cano, J. V. Heras, M. A. Lobo, E. Pinilla, E. Gutierrez and M. A. Monge, *Polyhedron*, 1989, **8**, 2727.
36 K. G. van Aswegen, J. G. Leipoldt, I. M. Potgieter, G. J. Lamprecht, A. Roodt and G. J. van Zyl, *Transition Met. Chem.*, 1991, **16**, 369.
37 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
38 G. M. Sheldrick, SHELXL 93, Program for refinement of crystal structures, University of Göttingen, 1993.

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