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Bridging alkyls in *d*-transition metal chemistry: reaction of $(cod)_2Rh_2(\mu\text{-}R)_2$ with Lewis bases to give (cod)Rh(R)(L) and their reaction with aromatic hydrocarbons

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Abstract

Low temperature (−70 °C) reaction of $(cod)_2Rh_2(\mu\text{-}Cl)_2$ with two molar equivalents of RLi in diethyl ether gives $(cod)_2Rh_2(\mu\text{-}R)_2$ where R = Me, Me_3SiCH_2. Even though the bridging alkyls are air and moisture sensitive, they may be stored for prolonged periods at −30 °C. The bridging alkyls are fluxional at +20 °C and the NMR spectra are consistent with a dimer of idealized D_{2h} symmetry. Low temperature NMR spectroscopic studies suggest that the dimers have idealized C_{2v} symmetry as found by X-ray studies described earlier. The bridging alkyls readily react with Lewis bases to give monomeric (cod)Rh(R)(L) where R = Me and L = PMe_3, PEt_3, $P(NMe_2)_3$, $P(OMe)_3$, py and R = Me_3SiCH_2, L = $P(OMe)_3$. The five coordinate, fluxional complex, (cod)RhMe$(PMe_3)_2$ also may be isolated. The four coordinate (cod)RhMe(PEt_3), slowly reacts with toluene to give (cod)Rh(*m*-tolyl)(PEt_3), (cod)Rh(*p*-tolyl)(PEt_3), and methane and (cod)RhMe(PMe_3) slowly reacts with benzene to give (cod)Rh(Ph)(PMe_3) and methane.

Bridging alkyl groups are a common and important feature in main group organometallic chemistry, common examples being $Li_4(\mu\text{-}Me)_4$, polymeric $BeMe_2$, and $Al_2Me_4(\mu\text{-}Me)_2$ [1]. Even copper(I) forms compounds such as $Cu_4(\mu\text{-}CH_2SiMe_3)_4$ [1c]. The bridge bonding is the result of overlap of a σ-molecular orbital of the CR_3 fragment and its electron with the σ-symmetry orbitals on each metal fragment generating multi-center molecular orbitals [2]. In contrast, bridging alkyls in *d*-transition metal chemistry are relatively rare, the largest number of examples being found in manganese and rhenium [3] though other metals do form

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compounds with bridging alkyl groups [4]. The principal reactivity pattern of bridging alkyls of the main group metal compounds consists of bridge cleavage reactions with either Lewis bases to give mononuclear coordination compounds or reaction with lithium alkyls to give anionic addition or "ate" complexes [1a]. A few analogous studies done on the manganese and rhenium alkyls show that they behave like the main group alkyls [3].

The bridging methyl compound of rhodium, $(cod)_2Rh_2(\mu\text{-}Me)_2$, was prepared and characterized by X-ray crystallography several years ago [4f]. The structure in the solid state is folded about the edge formed by intersection of two square planar rhodium fragments, $codRhMe_2$, at the bridging methyl carbon atoms, the dihedral angle between the intersection of these two planes being 104°. The geometry of the rhodium methyl is similar to that of the related nickel compound, $(\eta^3\text{-}1,3\text{-}Me_2C_3H_3)_2Ni_2(\mu\text{-}Me)_2$ [4e]. In this paper we describe full synthetic details for $(cod)_2Rh_2(\mu\text{-}R)_2$, where R is Me or Me_3SiCH_2, and their reactions with a variety of phosphines. In a latter paper we will describe the reactions of the bridging alkyls of rhodium and iridium with alkyllithium reagents.

Results and discussion

The full synthetic details for preparing the bridging methyl, $(cod)_2Rh_2(\mu\text{-}Me)_2$, and trimethylsilylmethyl, $(cod)_2Rh_2(\mu\text{-}CH_2SiMe_3)_2$, compounds of rhodium (eq. 1) are given in the Experimental Section. Both compounds are thermally sensitive and

$$(cod)_2Rh_2(\mu\text{-}Cl)_2 + 2RLi \xrightarrow[-70\,^\circ C]{Et_2O} (cod)_2Rh_2(\mu\text{-}R)_2 + 2LiCl \quad (1)$$

the temperature must be kept at −70 °C during the synthesis and isolation procedure. Both alkyls are very soluble in diethyl ether and they may be crystallized from a small amount of that solvent at −70 °C as yellow (R = Me) or orange ($R = CH_2SiMe_3$) crystals. Once isolated the compounds may be stored for days at −30 °C in absence of air and moisture. The methyl derivative is not stable enough to yield a satisfactory combustion analysis though the Me_3SiCH_2 derivative gives a satisfactory combustion analysis. At 0 °C in solution, C_6D_6 or C_7D_8, the solutions darken over several hours and alkane, MeH or Me_4Si, is eliminated. Examination of the alkanes by ^1H NMR spectroscopy shows that they do not incorporate deuterium from solvent, suggesting that the thermal decomposition does not involve free radicals.

As mentioned earlier, the bridging methyl has a folded structure in the solid state with idealized C_{2v} symmetry. The ^1H NMR spectrum at −70 °C is consistent with this geometry in solution since there are two chemically inequivalent cod-olefinic resonances which appear as single, slightly broadened resonances (presumably due to unresolved coupling rather than to chemical exchange) at δ 4.05 and 3.72 ppm. These coalesce at δ 3.90 ppm by 0 °C [5*]. The cod-aliphatic resonances appear as two broadened multiplets at both temperatures (−70 and −10 °C) at δ 2.38 and 1.78 ppm. The multiplets are due to unresolved coupling and small differences in chemical shift between the magnetically inequivalent cod-aliphatic protons. The bridging methyl appears as a single resonance at δ −1.55 ppm at 0 and −70 °C;

* This and other references marked with asterisks indicate notes occurring in the list of references.

apparently coupling to the rhodium nuclei is small with respect to the natural line width. The low temperature ^{13}C NMR spectrum also is consistent with the solid state structure since at $-40\,^{\circ}C$ the cod-olefinic resonances appear as two doublets, J(CH) 156 Hz in each case, at δ 78.6 and 72.4 ppm. The cod-aliphatic resonances appear as an apparent triplet (implying that the chemical shift difference between the chemically inequivalent carbons is small), J(CH) 128 Hz, at δ 31.5 ppm and the bridging methyl is a quartet of triplets with J(CH) 118 Hz and J(CRh) 19 Hz at δ 5.2 ppm.

The trimethylsilylmethyl compound appears to be structurally related to the methyl since the ^{1}H NMR spectrum at $-50\,^{\circ}C$ shows two types of cod-olefinic resonances at δ 4.02 and 3.94 ppm which give a single resonance at $0\,^{\circ}C$ at δ 4.00 ppm. The four cod-aliphatic resonances at $-50\,^{\circ}C$ at δ 2.49, 2.38, 1.87 and 1.60 ppm merge to two resonances at δ 2.45 and 1.78 ppm at $0\,^{\circ}C$. The Me_3Si resonance is a singlet at all temperatures at δ 0.25 and the bridging methylene is at δ -2.30, again showing no coupling to the rhodium nuclei. The ^{13}C NMR spectrum also is consistent with a dimeric, folded structure at $-30\,^{\circ}C$, since the cod-olefinic doublet resonances with J(CH) 146 Hz are not equivalent, δ 79.4 and 76.0 ppm and the cod-aliphatic resonances appear as an apparent triplet at δ 31.3 ppm with J(CH) 125 Hz. The Me_3Si carbons appear as a quartet with J(CH) 125 Hz at δ 6.0 ppm, and the bridging methylene is a triplet of triplets at δ 10.6 ppm with J(CH) 106 Hz and J(CRh) 17 Hz.

The two bridging alkyls are clearly fluxional. An intramolecular process that is consistent with the limited data currently available is one in which the C_{2v} molecule interconverts by way of a planar species with D_{2h} symmetry. The details of the process are difficult to study owing to the sensitivity of the compounds. In order to gain a qualitative understanding of the molecularity of the process, we mixed the two alkyls in a ^{1}H NMR tube and observed resonances from both alkyls as well as new resonances which may be ascribed to a mixed alkyl, $(cod)_2Rh_2(\mu\text{-}Me)(\mu\text{-}CH_2SiMe_3)$, indicating that the fluxional process could be intermolecular. Much more work is required to establish the mechanism for the chemical exchange, though it is noteworthy that the favored mechanism for bridge-terminal exchange in aluminum alkyls is an intermolecular one [6].

Not unexpectedly [7] reaction of lithium alkyls which contain β-hydrogens, EtLi and i-PrLi, with $(cod)_2Rh_2(\mu\text{-}Cl)_2$ at low temperatures lead to decomposition, giving olefin and the hydride, $(cod)_4Rh_4(\mu\text{-}H)_4$ [8]. Rather more curious is the observation that neopentane is the only identifiable product from the reaction of Me_3CCH_2Li and $(cod)_2Rh_2(\mu\text{-}Cl)_2$ at $-70\,^{\circ}C$.

Alkyls derived from the norbornadiene (nbd) complex, $(nbd)_2Rh_2(\mu\text{-}Cl)_2$, appear to be less thermally stable than those derived from $(cod)_2Rh_2(\mu\text{-}Cl)_2$. Thus, solutions resulting from addition of two molar equivalents of MeLi to $(nbd)_2Rh_2(\mu\text{-}Cl)_2$ begin to eliminate MeH by $-30\,^{\circ}C$ and the methyl compound could not be isolated. The trimethylsilylmethyl, presumably $(nbd)_2Rh_2(\mu\text{-}CH_2SiMe_3)_2$, is somewhat more thermally stable though the alkyl could not be obtained in pure form. The ^{1}H NMR spectrum ($20\,^{\circ}C$) is consistent with this formulation since the norbornadiene resonances appear at δ 3.75 (olefinic), δ 3.65 (bridgehead), δ 1.28 (aliphatic), the Me_3Si at 0.35 and the methylene appears at -2.30, all of which are singlets.

As previously described, $(cod)_2Ir_2(\mu\text{-}Cl)_2$ shows different behavior relative to

that of the rhodium analogue since reaction with MeLi gives the bridging methylene, $(cod)_2Ir_2(\mu\text{-}CH_2)_2$, rather than the bridging methyl. The mechanism of this process is unknown; following the reaction by variable temperature ^1H NMR spectroscopy shows that the reaction is complex, though the bridging methylene is isolated in decent (30–40%) yield. Even in the presence of one molar equivalent of PMe_3, the yellow $(cod)_2IR_2(\mu\text{-}CH_2)_2$ is the only product isolated. It is noteworthy that $(Me_3P)_6Ru_2(\mu\text{-}CH_2)_3$ is one of the products isolated from reaction of $Ru_2(O_2CMe)_4Cl$ with Me_2Mg and PMe_3 [10]; methyl groups being the source of methylene ligands.

Both bridging alkyls of rhodium react with Lewis bases to give sixteen-electron square planar complexes, (cod)Rh(R)(L), eq. 2, and in a few cases eighteen-electron, five coordinate complexes $(cod)Rh(R)(L)_2$. These complexes also may be prepared by a rather more traditional synthetic route as shown in eq. 3. The latter reaction is

$$(cod)_2Rh_2(\mu\text{-}R)_2 + 2L \rightarrow 2(cod)Rh(R)(L) \quad (2)$$

$$(cod)Rh(Cl)(L) + RLi \rightarrow (cod)Rh(R)(L) + LiCl \quad (3)$$

very convenient synthetically since (cod)Rh(Cl)(L) can be generated readily from the dimer, $(cod)_2Rh_2(\mu\text{-}Cl)_2$, by addition of one molar equivalent of a Lewis base per rhodium in toluene at $-70\,^\circ C$ followed by addition of the appropriate alkyl lithium. The $(cod)Rh(Cl)(PPh_3)$ complexes are well-known as are the alkyls, $(cod)Rh(R)(PPh_3)$, where R is Me, Ph, CH_2Ph, or C_6F_5 [11]. As noted above, attempted preparation of the iridium phosphine complex, $(cod)IrMe(PMe_3)$, gives $(cod)_2Ir_2(\mu\text{-}CH_2)_2$, though $(cod)Ir(CH_2SiMe_3)(PMe_3)$ can be made by a route analogous to that shown in eq. 3.

The ^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectra are shown in Table 1 and the synthetic details are in the Experimental Section for the four coordinate rhodium complexes. The spectroscopy is consistent with a molecule of idealized C_s symmetry; the plane passing through the mid-point of each cod-olefin bond and containing the Rh, L, and CR_3 atoms. The cod-olefin resonances in the ^1H and ^{13}C NMR spectra are chemically inequivalent as are the cod-aliphatics. The former resonances appear as sharp singlets and the latter are multiplets due to unresolved coupling to the other $I = 1/2$ nuclei in the ^1H NMR spectra. The ^{13}C NMR spectra in the cod-olefinic region appear as a doublet of doublets of doublets with $J(CH)$ of ca. 150 Hz, $J(CP)$ of 10 to 16 Hz and $J(CRh)$ of 7 to 14 Hz. This resonance presumably arises from the cod-olefin position *trans* to the phosphine when $L = PR_3$ since the other cod-olefin resonance appears as a doublet with $J(CRh)$ of ca. 8 Hz and $J(CP)$ being small relative to the line width. This latter resonance is most reasonably ascribed to the cod-olefin position *trans* to the alkyl or aryl group. Further, in $(cod)Ir(CH_2SiMe_3)(PMe_3)$ the cod-olefin resonances, in the $^{13}C\{^1H\}$ NMR spectrum appear as a doublet, $J(CP) = 16$ Hz and as a singlet. In other similar compounds of Rh and Ir, $J(CP) > J(CRh)$ [12], so in Table 1 the largest coupling is assigned to $J(CP)$. The values could be reversed since both values are small and approximately equal. The cod-aliphatic resonances appear as apparent triplets with $J(CH)$ of ca. 120 Hz and the $J(CRh)$ is not resolved.

On adduct formation the ^1H NMR resonance for the alkyl group is deshielded by one to two ppm and $J(HRh)$ increases to ca. 1.5 Hz from a very small value in the bridging alkyl. No trend is observed in the ^{13}C NMR spectrum other than the

(Continued on p. 111)

Table 1

NMR spectral data [a] for (cod)Rh(R)(PR'_3)

	R	PR'_3	cod-olefin	cod-aliphatic
(cod)Rh(Me)(PMe_3) (R = Me; R′ = Me)				
^1H	0.32dd	0.86dd	5.09s	2.22m
	J(HP) 6.2, *J*(HRh) 1.5	*J*(HP) 7.5, *J*(HRh) 1.2	3.84s	2.04m
$^{13}C\{^1H\}$	4.8dd	14.5d	95.0dd	32.6s
	J(CP) 13, *J*(CRh) 25	*J*(CP) 23	*J*(CP) 12, *J*(CRh) 9.1	31.2s
			77.2d	
			J(CRh) 7.6	
$^{31}P\{^1H\}$	−13.80d			
	J(PRh) 175			
(cod)RhMe(PEt_3) (R = Me; R′ = Et)				
^1H	0.11dd	1.33, 5 lines	4.92s	2.10m
	J(HP) 4, *J*(HRh) 1.5	Separation 7	3.85s	2.00m
		0.90, 5 lines		
		Separation 7		
^{13}C	4.7 qdd	15.1qd	9.9ddd	32.6t
	J(CP) 12, *J*(CRh) 26	*J*(CP) 20.8, *J*(CH) 126	*J*(CP) 9.5, *J*(CRh) 9.5	*J*(CH) 126
	J(CH) 122	8.80t	*J*(CH) 153	31.2t
		J(CH) 127	77.8dd	*J*(CH) 126
			J(CRh) 7, *J*(CH) 153	
$^{31}P\{^1H\}$	18.38d			
	J(PRh) 174			
(cod)RhMe[$P(OMe)_3$] (R = Me; R′ = OMe)				
^1H	0.26dd	3.44d	5.24s	2.1m
	J(HP) 4.2, *J*(HRh) 1.5	*J*(HP) 12	4.29s	
$^{13}C\{^1H\}$	−0.30dd	51.0s	104.1dd	32.2m
	J(CP) 14, *J*(CRh) 23		*J*(CP) 16, *J*(CRh) 6.7	30.7m
			80.2d	
			J(CRh) 6.4	
$^{31}P\{^1H\}$	139.8d			
	J(PRh) 307			
(cod)RhMe[$P(NMe_2)_3$] (R = Me; R′ = NMe_2)				
^1H	0.28dd	2.54d	4.87s	2.2m
	J(HP) 4.1, *J*(HRh) 1.7	*J*(HP) 8.6	4.30s	2.0m
$^{13}C\{^1H\}$	2.73dd	39.1d	94.9dd	32.5s
	J(CP) 9.8, *J*(CRh) 25.3	*J*(CP) 10	*J*(CP) 15, *J*(CRh) 8.6	30.7s
			76.3d	
			J(CRh) 7.4	
$^{31}P\{^1H\}$	126.7d			
	J(PRh) 245			
(cod)RhMe(py) (R = Me, PR'_3 = py)				
^1H	0.07br,s	8.35m(2)	4.21s	2.4m
		6.79m(1)	3.70s	1.9m
		6.45m(2)		
$^{13}C\{^1H\}$	10.2d	150.8, 135.5	86.1d	33.0s
	J(CRh) 26.8	124.8	*J*(CRh) 5.7	30.9s
			73.8d	
			J(CRh) 14	

continued

Table 1 (continued)

	R	PR'_3	cod-olefin	cod-aliphatic
(cod)Rh(CH_2SiMe_3)[P(OMe)$_3$] (R = CH_2SiMe_3, R′ = OMe)				
^1H	0.43dd (CH_2)	3.38d	5.16s	2.1m
	J(HP) 5.7, *J*(HRh) 1.5	*J*(HP) 12	4.13s	
	0.36s (Me_3Si)			
$^{13}C\{^1H\}$	9.9dd (CH_2)	51.0s	99.9dd	32.1s
	J(CP) 13, *J*(CRh) 23		*J*(CP) 17, *J*(CRh) 8	30.9s
	4.5s (Me_3Si)		80.4d	
			J(CRh) 6	
$^{31}P\{^1H\}$	134.4d			
	J(PRh) 310			
(cod)Rh(CH_2CMe_3)(PMe$_3$) (R = CH_2CMe_3; R′ = Me)				
^1H	1.20dd (CH_2)	0.96dd	4.72s	2.1m
	J(HP) 9, *J*(HRh) 1.7	*J*(HP) 6.6, *J*(HRh) 1	3.88s	2.0m
	1.36s (CMe_3)			
$^{31}P\{^1H\}$	−21.0d			
	J(PRh) 182			
(cod)Rh(Ph)(PMe$_3$) (R = Ph; R′ = Me)				
^1H	7.70, *o*-H	0.68dd	5.03m	2.19m
	J(HH) 7.2	*J*(HP) 7.8, *J*(HRh) 1.4	4.00m	2.02m
	7.25, *m*-H			
	J(HH) 7.2			
	7.03, *p*-H			
	J(HH) 7.2			
$^{13}C\{^1H\}$	177.4dd, i-C	14.2dd	96.2dd	31.6d
	J(CP) 15.4, *J*(CRh) 31.6	*J*(CP) 25, *J*(CRh) 1.8	*J*(CP) 12.3, *J*(CRh) 8.5	*J*(CP) 2.4
	137.4d, *o*-C		81.3d	31.1s
	J(CRh) 3.5		*J*(CRh) 7.2	
	126.7d, *m*-C			
	J(CRh) 1.3			
	121.3s, *p*-C			
$^{31}P\{^1H\}$	−17.3d			
	J(PRh) 178			
(cod)Rh(m-tolyl)PEt$_3$ (R = m-tolyl; R′ = Et)				
^1H	7.47s, *o*-H	1.14dqm (CH_2)	4.88s	2.22m
	7.40d, *o*-H	*J*(HP) = *J*(HH) = 7.3	4.09s	2.04m
	J(HH) 7.3	0.89dt (CH_3)		
	7.08t, *m*-H	*J*(HP) 14.8, *J*(HH) 7.3		
	J(HH) 7.3			
	6.74m, *p*-H			
	J(HH) 7.3			
	2.32s, *m*-Me			
$^{13}C\{^1H\}$	176.8dd, *i*-C	14.7d (CH_2)	99.5dd	32.2s
	J(CP) 15, *J*(CRh) 31	*J*(CP) 22	*J*(CP) = *J*(CRh) 10	
	137.5d, *o*-C	6.64s (CH_2)	81.8d	31.5s
	J(CRh) 2.5		*J*(CRh) 6.9	
	134.7s, *m*-C			
	134.0d, *o*-C			
	J(CRh) 2.6			
	126.4s, *m*-C			
	122.3s, *p*-C			
	22.0s, *m*-Me			
$^1P\{^1H\}$	14.0d			
	J(PRh) 176			

Table 1 (continued)

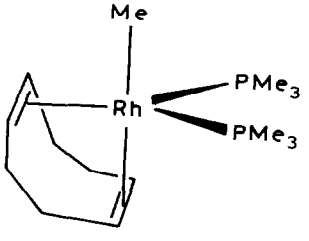
	R	PR'_3	cod-olefin	cod-aliphatic
(cod)Ir(CH_2SiMe_3)(PMe_3) (R = CH_2SiMe_3; R′ = Me)				
^1H	1.10d (CH_2)	0.98d	4.57s	2.1m
	J(HP) 9	*J*(HP) 8	2.92s	1.7m
	0.31s ($SiMe_3$)			
$^{13}C\{^1H\}$	17.5d (CH_2)	14.9d	82.3d	33.4s
	J(CP) 7	*J*(CP) 31	*J*(CP) 16	32.3s
	5.7s ($SiMe_3$)		59.9s	

[a] The spectra were recorded at 20 °C in either C_6D_6 or C_7D_8, except for (cod)Rh(*m*-tolyl)(PEt_3) which was recorded in C_6D_{12}. The chemical shifts are in δ-units and *J* is in Hertz.

strong dependence of the chemical shift of the alkyl carbon on the identity of the Lewis base; the chemical shift spans the range δ 10.2 (L = py) to −0.30 ($P(OMe)_3$) ppm. The value of *J*(CRh) increases on adduct formation from ca. 20 to ca. 25 Hz.

The $^{31}P\{^1H\}$ NMR spectra of the mono-phosphine complexes are doublets in which *J*(PRh) varies from 175 to 307 Hz for a given alkyl group though the value of *J*(PRh) does not appreciably change with the identity of the direct-bound alkyl group. For the complexes in Table 1, *J*(PRh) increases in the order $PMe_3 = PEt_3 < P(NMe_2)_3 < P(OMe)_3$. A similar trend was noted for complexes of the type $[(Me_3C)_2PCH_2CH_2P(CMe_3)_2]RhCl(PR_3)$ and rationalized on the basis of the steric size of the group bound to phosphorus and its electronegativity since both effects change the amount of *s*-character of the phosphorus donor orbital and therefore *J*(PRh) [13].

The methyl, (cod)Rh(Me)(PMe_3), takes up an additional molar equivalent of PMe_3 to give the yellow five-coordinate (cod)RhMe(PMe_3)$_2$. This molecule is a new member of the series of compounds (diene)RhMe(L)$_2$ and (diene)IrMeL$_2$ prepared by Osborn and Shapley in their seminal studies on fluxional organo-transition metal complexes [14]. Using NMR spectroscopy in conjunction with X-ray crystallography [15] these authors showed that the ground state structure of these complexes is a trigonal bipyramid with the best σ-donor, the Me, on the apical site and the other apical site being occupied by one of the arms of the chelating diene. The remaining olefinic group of the diene is on an equatorial site, lying co-linear with the equatorial plane and the mono-dentate ligands occupying the other two equatorial sites so that the molecule has idealized C_s symmetry. By analogy, the new complex codRhMe(PMe_3)$_2$ has a similar structure:



The structural assignment is consistent with ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR data. Intermolecular phosphine exchange occurs which is fast on the NMR time scale at room temperature but slow at −15 °C. The equivalent phosphines resonate

as a doublet at δ 18.07 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The phosphorus–rhodium coupling constant, J(PRh) 122.8 Hz, is about 50 Hz smaller than the values observed for the (cod)Rh(PR_3)X complexes, see Table 1. In both the ^1H and $^{13}C\{^1H\}$ spectra, the phosphines appear as virtual triplets. The methyl group is coupled to both rhodium and the equivalent phosphorus nuclei in the proton spectrum with δ −0.21 and appearing as a triplet of doublets with J(HP) 11.7 and J(HRh) 1.8 Hz, and in the carbon spectrum, appearing as a five line pattern with J(CP) 11.2 and J(CRh) 21.8 Hz. Perhaps the most interesting feature of the ^1H NMR spectrum is the appearance of the cyclooctadiene protons as six resolved resonances at 500 MHz. The vinylic group in the equatorial plane appears as a multiplet at δ 3.72 ppm, and the other vinyl group resonates at δ 2.72 ppm. The methylene protons of the cod ligand appear as four multiplets at δ 2.6, 2.4, 2.25, and 2.2 ppm. These observations agree qualitatively with the spectra of the analogous (cod)M(PR_3)X species prepared by Shapley and Osborn. If the NMR sample temperature is increased to 20 °C, the proton resonances of trimethylphosphine and of the rhodium-bound methyl group lose their fine structure. The methyl resonance is very broad at this temperature. At 45 °C these two signals become narrower and take on the appearance of doublets. Thus, the methyl signal loses coupling to phosphorus, and the phosphine signals lose virtual P–P coupling. The proton resonances for the cod ligand are relatively unaffected by the increase in temperature. This behavior is indicative of rapid intermolecular phosphine exchange.

Similar behavior was seen by Shapley and Osborn in their series of diene compounds. However, in some cases they observed a second dynamic process in the ^1H NMR which caused coalescence of the vinyl signals of the diene ligand. This process caused no change in the phosphine or methyl resonances and generally takes place at a lower temperature than does the intermolecular phosphine exchange. By observing the second process in molecules containing phosphine ligands with diastereotopic methyl groups [e.g., (cod)Ir($PMe_2Ph)_2$Me], Osborn's group concludes that the net effect of this intramolecular transformation is to interchange the nonequivalent double bonds of the diene without interchanging the phosphine ligands. Viewed simply, the process may be pictured as a rotation of the diene about its own C_2 axis as the rest of the molecule remains fixed. For (cod)RhMe($PMe_3)_2$ and other (cod)RhMeL_2 species, the "diene rotation" process is not observed.

Attempts to prepare the analogous compounds (cod)RhCl($PMe_3)_2$, (cod)-RhPh($PMe_3)_2$, and (cod)RhMe($PEt_3)_2$ resulted in the isolation at room temperature of mixtures containing ($PR_3)_3$RhX and (cod)RhX(PR_3) species (for R = Me, X = Cl, Ph; for R = Et, X = Me). An apparent disproportionation reaction (eq. 4) occurs for these combinations of ligand and the substituent. The compounds

$$2(\text{cod})\text{Rh(X)}(PR_3)_2 \rightarrow (\text{cod})\text{Rh(X)}(PR_3) + (PR_3)_3\text{RhX} + \text{cod} \qquad (4)$$

(cod)RhMe($PEt_3)_2$ and (cod)RhPh($PMe_3)_2$ may be generated at −70 °C and observed by NMR spectroscopy by the addition of one molar equivalent of phosphine to the corresponding square planar complexes. The two compounds are readily identified by the appearance of doublets with phosphorus–rhodium coupling constants of about 120 Hz in their $^{31}P\{^1H\}$ NMR spectra, see Experimental Section for details. In the case of (cod)RhMe($PEt_3)_2$ the ^1H and $^{31}P\{^1H\}$ spectra show the five-coordinate compound [along with 8–10% of (cod)RhMe(PEt_3)]. There is no sign of increasing disproportionation to ($PEt_3)_3$RhMe and (cod)RhMe(PEt_3) as the

temperature is raised to +10 °C. In the case of the phenyl complex, (cod)-$RhPh(PMe_3)_2$ is the dominant compound as it is clearly visible at −71 and −50 °C along with (cod)$RhPh(PMe_3)$ and $(PMe_3)_3PhPh$. As the temperature is increased to +10 °C the resonances of the pentacoordinate compound steadily disappear as those of the four-coordinate compounds become more intense. Also, the proton resonances of free cyclooctadiene become more intense as (cod)$RhPh(PMe_3)_2$ disproportionates. These results indicate the following sequence for decreasing stability of (cod)$RhX(PR_3)_2$ species with respect to disproportionation: (cod)$RhMe(PMe_3)_2$ > (cod)$RhPh(PEt_3)_2$ > (cod)$RhPh(PMe_3)_2$ > (cod)$RhCl(PMe_3)_2$. The relative instability of the phenyl and chloro compounds is not surprising in view of the different electronic effects of these substituents relative to the methyl group. The reason for the reduced stability of (cod)$RhMe(PEt_3)_2$ relative to (cod)$RhMe(PMe_3)_2$ is not obvious. The cone angle [16] of PEt_3 is 132°, compared to 118° for PMe_3, so that one may suggest an explanation based on steric constraints. However, Rice and Osborn isolated the complex (cod)$RhMe(PMePh_2)_2$ at 0 °C [14b], and the cone angle for $PMePh_2$ is reported to be 136°, even larger than that of PEt_3 [16]. Although attempted isolation of (cod)$RhMe(PEt_3)_2$ has resulted in the disproportionation products, the mixed phosphine analog (cod)$RhMe(PEt_3)(PMe_3)$ may be isolated in a mixture with (cod)$RhMe(PMe_3)_2$ and (cod)$RhMe(PEt_3)$. The mixed phosphine compound is readily characterized by the two well separated doublet of doublet resonances in the $^{31}P\{^1H\}$ NMR spectrum and by the ddd pattern for the rhodium-bound methyl group in the proton spectrum. The stability of (cod)$RhMe(PEt_3)(PMe_3)$ relative to (cod)$RhMe(PEt_3)_2$ supports the steric argument based on cone angles mentioned above for the stability of pentacoordinate compounds with respect to disproportionation.

Not surprisingly, the variable temperature ^1H and $^{31}P\{^1H\}$ NMR spectra of (cod)$RhMe(PEt_3)_2$ and (cod)$RhPh(PMe_3)_2$ show signs of dynamic behavior. The fluxional processes in (cod)$RhMe(PEt_3)_2$ and (cod)$RhPh(PMe_3)_2$ are difficult to study since disproportionation is extensive at temperatures greater than −10 °C. However, at −50 °C, both five coordinate compounds are stereochemically rigid with a structure similar to (cod)$RhMe(PMe_3)_2$.

It was of interest to inquire into the reaction or lack thereof, of these simple rhodium (I), d^8, alkyl systems with hydrocarbons since it is now emerging that a common reactivity pattern of organorhodium compounds is their ability to activate aromatic and aliphatic C–H bonds [17].

Heating (cod)$Rh(Me)(PEt_3)$ at 70 °C in a sealed NMR tube in either toluene-d_8 or toluene-d_0 and monitoring the course of the reaction by $^{31}P\{^1H\}$ NMR spectroscopy at +20 °C shows that the methyl compound is slowly converted, $t_{1/2}$ 21 h at 70 °C, into two principal species. These two species show AX patterns, A = ^{31}P and X = ^{103}Rh, in the $^{31}P\{^1H\}$ NMR spectra at δ 14.4 ppm, J (PRh) 176 Hz, and δ 14.2 ppm, J(PRh) 176 Hz, in a 1.0/2.0 ratio. The latter feature is identical to that of an authentic sample of (cod)Rh(*m*-tolyl)(PEt_3) and the former is probably (cod)Rh(*p*-tolyl)(PEt_3) though we have not prepared this compound in the pure state. Observation of the solution after ca. 21 h by ^1H NMR spectroscopy shows that methane is evolved and when the reaction solvent is toluene-d_8 the methane is CH_3D, which appears as a 1/1/1 triplet at δ 0.16 ppm. After ca. 28 h, CH_4, δ 0.18 ppm, is also formed. After ca. one half-life in toluene-d_8, a feature appears in the $^{31}P\{^1H\}$ NMR spectrum that is a doublet, I, δ 27.0 ppm and J(PRh) 195 Hz. In

non-deuterated toluene, the same doublet due to I appears along with a pair of doublet of doublets, II (the AB portion of an ABX spin system) in the spectrum centered at δ 25.0 ppm. After 21 h, the two unidentified species I and II, account for 21% of the total intensity in the ^{31}P NMR spectrum.

Heating (cod)Rh(Me)(PMe_3) in a sealed NMR tube in either benzene-d_6 or benzene-d_0 at 60 °C and monitoring the sample periodically by $^{31}P\{^1H\}$ NMR spectroscopy (+20 °C) shows that (cod)Rh(Ph)(PMe_3) or its C_6D_5 analogue is obtained with $t_{1/2}$ of ca. 100 h (60 °C) in C_6D_6 and ca. 31 h (60 °C) in C_6H_6. Two unidentified species I′ and II′ are also obtained in non-deuterated solvents; $\delta_{I'}$ −10.5 ppm with J(PRh) 195 Hz and II′ appears as the AB portion of a ABX spin system. In deuterated solvents only I′ is obtained with δ_I −11.9 ppm and J(PRh) 193 Hz. The species I′ and II′ account for ca. 18% of the total phosphorus intensity after 76 h in C_6D_6. The methane evolved is predominately CH_4. In C_6H_6, the compound identified as I′ comprises 29% of all the phosphorus intensity after 5 h at 80 °C.

Heating (cod)Rh(Me)(PEt_3) in cyclohexane-d_{12} in a sealed NMR tube for 80 h at 70 °C, then cooling to 20 °C and monitoring the $^{31}P\{^1H\}$ NMR spectrum shows resonances due to starting material and I and II. The latter two resonances account for ca. 20% of the total intensity in the phosphorus resonances. The ^1H NMR spectrum shows CH_4 and no detectable CH_3D. Similar results are obtained with Me_4Si (neat) and $^{13}CH_4$ in cyclohexane-d_{12} at 70 °C for 17 h showed that ca. 20% of the starting material is converted to I′ and II′. It is noteworthy that storing (cod)Rh(Me)(PMe_3) at 20 °C for two months in the solid state in absence of air and moisture or in C_6D_6 solution in a sealed NMR tube at 20 °C for several months results in the appearance in the $^{31}P\{^1H\}$ NMR spectrum of resonances due to I′ and II′.

The compounds of I and II, or I′ and II′, are not products of arene activation, eq. 5 and 6, but are derived from elimination of MeH from the cod-alkyls. Perhaps

$$(cod)RhMe(PR_3) + C_6H_5R \rightarrow (cod)Rh(C_6H_4R)(L) + MeH \quad (5)$$

(R = H, Me)

$$(cod)RhMe(PR_3) + C_6D_5R \rightarrow (cod)Rh(C_6D_5R)(L) + MeD \quad (6)$$

($R = D, CD_3$)

it is not unreasonable to suggest that I(I′) is derived by H-abstraction from a phosphine analogous to $(Me_3P)_4Rh_2(CH_2PMe_2)_2$ [18] and that II(II′) is derived from H-abstraction from cod. Further speculation is meaningless since we have not been able to isolate these materials in pure form nor have we been able to develop suitable synthetic routes to them.

These studies show that these simple four coordinate rhodium(I) d^8 alkyls can activate arene C–H bonds, albeit at very slow rates. Since the rates are slow other processes compete with C–H activation. Accordingly, the systems are messy and speculation as to mechanism is not warranted. Further studies on related systems will be published in due course.

Experimental

All manipulations were carried out under nitrogen or argon by using standard Schlenk techniques or in a Vacuum Atmospheres inert atmosphere box. Elemental

analyses were done in the Microanalytical Laboratory of this department. Nuclear magnetic resonance spectra were recorded on a Bruker AM 500 spectrometer operating at 500 MHz (^{1}H) or on homebuilt machines operating at 180, 200, or 250 MHz (^{1}H). Chemical shifts were referenced to Me_4Si for ^1H $^{13}C\{^1H\}$ spectra, $\delta = 0$ and positive chemical shifts are to high frequency. The ^{31}P chemical shifts were initially referenced to $(MeO)_3PO$, then converted to 85% H_3PO_4, $\delta = 0$ and positive shifts are to high frequency. Mass spectra were determined on an AEI MS-12 (electron impact) and on a Finnigan 400 (chemical ionization).

$(cod)_2Rh_2(\mu\text{-}Me)_2$. Methyllithium (0.65 ml of a 1.3 *M* diethyl ether solution, 0.84 mmol) was added to $(cod)_2Rh_2(\mu\text{-}Cl)_2$ [19] (0.20 g, 0.40 mmol) in diethyl ether (200 ml) at −70 °C. The suspension was stirred at this temperature for 2 h then filtered. The diethyl ether was removed from the filtrate under reduced pressure at −70 °C. When a few ml of diethyl ether remained, yellow crystals appeared on the walls of the flask; these were allowed to grow at −70 °C. They were collected (−70 °C) and dried under reduced pressure (−70 °C) in a yield of 0.09 g (50%). The compound was stored at −30 °C. ^{1}H NMR (C_7D_8, 0 °C): δ 3.90 (s, cod-olefin, 4H), 2.38 (m, cod-aliphatic, 4H), 1.78 (m, cod-aliphatic, 4H), −1.55 (s, Rh–Me, 6H) ppm. ^{13}C NMR (C_7D_8, −40 °C): δ 78.6 (d, *J*(CH) 157 Hz, olefin), 72.4 (d, *J*(CH) 156 Hz, olefin), 31.5 (t, *J*(CH) 128 Hz, aliphatic), 5.2 (q, *J*(CH) 118 Hz, t, *J*(CRh) 19 Hz, Rh–Me).

$(cod)_2Rh_2(\mu\text{-}CH_2SiMe_3)_2$. The molecule was prepared similar to that of $(cod)_2Rh_2(\mu\text{-}Me)_2$ from $(cod)_2Rh_2(\mu\text{-}Cl)_2$ (0.40 mmol) and $LiCH_2SiMe_3$ (0.80 mmol) in diethyl ether at −70 °C in 80% yield. Anal. Found: C, 48.5; H, 7.64. $C_{24}H_{46}Rh_2Si_2$ calcd.: C, 48.3; H, 7.77%. ^{1}H NMR (C_7D_8, −50 °C): δ 4.02 (s, cod-olefin, 2H), 3.94 (s, cod-olefin, 2H), 2.49 (s, cod-aliphatic, 2H), 2.28 (s, cod-aliphatic, 2H), 1.87 (m, cod-aliphatic, 2H), 1.60 (m, cod-aliphatic, 2H), 0.25 (s, Me_3Si, 9H), −2.30 (s, Rh–CH_2, 2H ppm). ^{13}C NMR (C_7D_8, −30 °C): δ 79.4 (d, *J*(CH) 146 Hz, cod-olefin), 76.0 (d, *J*(CH) 146 Hz, cod-olefin), 31.3 (t, *J*(CH) 125 Hz, cod-aliphatic), 10.6 (t, *J*(CH) 106 Hz, of t, *J*(CRh) 17 Hz, Rh–CH_2), 6.00 (q, *J*(CH) 116 Hz, Me_3Si) ppm.

(cod)RhMe(PMe_3). (a) From $(cod)_2Rh_2(\mu\text{-}Me)_2$ and PMe_3. To a solution of $(cod)_2Rh_2(\mu\text{-}Me)_2$, generated from $(cod)_2Rh_2(\mu\text{-}Cl)_2$ (1.0 mmol) and MeLi in diethyl ether at −70 °C was added PMe_3 (2.1 mmol). The red-orange solution was warmed to room temperature and stirred for 2 h. The volatile material was removed under reduced pressure and the residue was crystallized as orange-red crystals in 61% (0.37 g) yield from pentane at −60 °C. Anal. Found: C, 47.8; H, 8.15; P, 10.3. $M^+ = 302$. $C_{12}H_{24}PRh$ calcd.: C, 47.7; H, 8.01; P, 10.2%.

(b) From (cod)RhCl(PMe_3) and MeLi. Trimethylphosphine (0.30 ml, 3.1 mmol) was added to a rapidly stirred suspension of $(cod)_2Rh_2(\mu\text{-}Cl)_2$ (0.73 g, 1.48 mmol) in toluene (125 ml) at −70 °C. A small amount of precipitate formed during the addition, but the bulk of the material remained in solution. After 5 min, MeLi (2.6 ml of a 1.3 *M* diethyl ether solution, 3.4 mmol) was added and the orange solution was stirred at −70 °C for 1 h then for an additional hour as the flask was allowed to warm to room temperature. The volatile material was removed under reduced pressure and the orange residue was extracted into pentane. After filtration, the extract was concentrated and the concentrate was crystallized by cooling to −70 °C. The orange crystals, whose NMR spectra were identical in all respects to those described in (a) above, were isolated in 71% (0.63 g) yield. The (cod)RhCl(PMe_3)

may be isolated by removing the toluene and extracting the yellow residue into CH_2Cl_2/Et_2O (1/1) and cooling to −70 °C to produce 0.49 g (42%) of golden crystals of (cod)RhCl(PMe_3). ^1H NMR (C_6D_6, 20 °C): δ 5.70 (s, cod-olefin, 2H), 3.18 (s, cod-olefin, 2H), 2.12 (m, cod-aliphatic, 4H), 1.72 (m, cod-aliphatic, 4H), 0.88 (d, *J*(HP) 9.3 Hz of d, *J*(HRh) 0.7 Hz, PMe_3, 9H) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ −7.58 (d, *J*(PRh) 148 Hz) ppm.

(cod)RhMe(PEt$_3$). This compound was prepared as in (*b*) above and was crystallized as orange-red crystals from pentane (−60 °C) in 76% yield. Anal. Found: C, 52.1; H, 8.73. $M^+ = 344$. $C_{15}H_{30}PRh$ calcd.: C, 52.3; H, 8.78%.

(cod)RhMe[P(OMe)$_3$]. This compound was prepared as in (*a*) above and was crystallized from pentane (−60 °C) in 86% yield. Anal. Found: C, 41.9; H, 6.98; P, 8.75. $C_{12}H_{24}O_3PRh$ calcd.: C, 42.1; H, 6.91; P, 8.83%.

(cod)RhMe[P(NMe$_2$)$_3$]. This material was prepared as in (*a*) above and was isolated as orange crystals from pentane (−70 °C) in 69% yield. Anal. Calcd for $C_{15}H_{33}N_3PRh$: C, 46.5; H, 8.56; N, 10.8; P, 7.95. Found: C, 45.9; H, 8.38; N, 10.6; P, 8.58. M^+: 389.

(cod)RhMe(py). This compound was prepared as in (*a*) above and crystallized as orange-yellow crystals from toluene : pentane (1/10) in 51% yield. Anal. Found: C, 55.2; H, 6.69; N, 4.95. $C_{14}H_{20}NRh$ calcd.: C, 55.1; H, 6.60; N, 4.59%.

(cod)Rh(Ph)(PMe$_3$). The phenyl compound was prepared from $(cod)_2Rh_2(\mu\text{-}Cl)_2$ and PMe_3 as in (*b*) above, then PhLi was added. Red-orange crystals were obtained from pentane (−70 °C) in 49% yield. Anal. Found: C, 56.0; H, 7.27; P, 8.63. $M^+ = 364$. $C_{17}H_{26}PRh$ calcd.: C, 56.0; H, 7.21; P, 8.50%.

(cod)Rh(m-tolyl)(PEt$_3$). This aryl was prepared analogous to that of (cod)Rh(Ph)(PMe_3), above, and crystallized as red-orange clumps from pentane (−70 °C). The complex could never be obtained analytically pure though a molecular ion at 420 was observed in the mass spectrum.

(cod)RhMe(PMe$_3$)$_2$. Trimethylphosphine (0.26 ml, 2.7 mmol) was added to a toluene (50 ml) suspension of $(cod)_2Rh_2(\mu\text{-}Cl)_2$ (0.302 g, 0.613 mmol) at −70 °C. After 10 min, MeLi (0.85 ml of a 1.6 *M* diethyl ether solution, 1.4 mmol) was added. After stirring for 10 min at −70 °C, the flask was allowed to warm to room temperature over 2 h. The volatile material was removed under reduced pressure and the yellow residue was crystallized from pentane (−70 °C) as yellow prisms in 52% (0.24 g) yield. Anal. Found: C, 47.9; H, 8.77; P, 16.2. $(M+1)^+$ by chemical ionization with $CH_4 = 379$. $C_{15}H_{33}P_2Rh$ calcd.: C, 47.6; H, 8.81; P, 16.4%. ^1H NMR (C_7H_8, −16 °C, 500 MHz): δ 3.72 (m, cod-olefin, 2H), 2.72 (m, cod-vinyl, 2H), 2.61 (m, cod-aliphatic, 2H), 2.40 (m, cod-aliphatic, 2H), 2.26 (m, cod-aliphatic, 2H), 2.20 (m, cod-aliphatic, 2H), 1.02 (virtual t, *N* 5 Hz, PMe_3, 18 H), −0.21 (t, *J*(HP) 11.7 Hz of d, *J*(HRh) 1.8 Hz, Rh–Me, 3H). $^{13}C\{^1H\}$ NMR (C_7H_8, −25 °C, 126 MHz): δ 84.4 (s, cod-olefin), 67.5 (ddd, *J*(CP) 62.7 Hz, *J*(CP) 36.6 Hz, *J*(CRh) 12.5, cod-olefin), 34.9 (s, cod-aliphatic), 32.9 (t, *J*(CP) 4.2 Hz, cod-aliphatic), 18.5 (virtual t, *N* 17.5 Hz, PMe_3), −4.59 (d, *J*(CRh) 21.8 Hz, of t, *J*(CP) 11.2 Hz, Rh–Me) ppm. $^{31}P\{^1H\}$ NMR (C_7H_8, −20 °C, 82 MHz): δ −18.07 (d, *J*(PRh) 123 Hz) ppm.

Arene activation studies. Samples were prepared in NMR tubes with 20–30 mg of the alkyl, 0.6 ml of solvent, and a sealed capillary tube containing a mixture of toluene-d_8 and $(MeO)_3PO$ (10/1) was placed inside the NMR tube. The NMR tube was exposed to a dynamic vacuum (−196 °C) and the tube was flame sealed.

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