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BASIC METALS

XXXIII *. SYNTHESIS AND REACTIVITY OF PENTAMETHYLCYCLOPENTADIENYLRHODIUM(I) COMPLEXES: METAL BASICITY VERSUS PHOSPHORUS BASICITY IN $C_5Me_5Rh(CO)P_2Me_4$

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Summary

$C_5Me_5Rh(CO)_2$ (I) reacts with PMe_3 and P_2Me_4 to give $C_5Me_5Rh(CO)PMe_3$ (II) and $C_5Me_5Rh(CO)P_2Me_4$ (VIII), respectively, in high yields. Reactions of II with acids HX yield stable salts IIIa—IIIc of the hydridorhodium cation $[C_5Me_5RhH(CO)PMe_3]^+$, whereas methyl and ethyl iodide give the acyl complexes $C_5Me_5RhI(COR)PMe_3$ (IV, V); the latter react with $AgPF_6$ to form $[C_5Me_5RhR(CO)PMe_3]PF_6$ (VI, VII). Treatment of the tetramethyldiphosphine complex VIII with MeI in 1 : 1 molar ratio yields $C_5Me_5RhI(COMe)P_2Me_4$ (X), which with excess MeI forms $[C_5Me_5RhI(COMe)P_2Me_5]I$ (XI). The syntheses of $[C_5Me_5RhMe(CO)P_2Me_4]X$ (XIIa: X = BF_4; XIIb: X = PF_6), $[C_5Me_5RhMe(CO)P_2Me_5](PF_6)_2$ (XIII) and the dinuclear rhodium(I) complex $[C_5Me_5Rh(CO)]_2(\mu\text{-}P_2Me_4)$ (IX) are also described.

Metal basicity has been a subject of general interest at least since the classical work of Vaska [3] on reactions of the d^8 metal complexes *trans*-$[MX(CO)L_2]$ (M = Rh, Ir; X = Cl, Br etc.; L = PR_3, AsR_3 etc.) with electrophiles. More recently we have been investigating the Lewis-base properties of another class of d^8 systems, namely C_5H_5MLL' (M = Co, Rh), in which the metal, by contrast to that in Vaska's compounds, possesses 18 instead of 16 electrons in the valence shell. These half-sandwich type complexes are, nevertheless, strong nucleophiles, and react with a variety of electrophiles EX (e.g. HX, RX, RCOX, R_3SnX, $ZnCl_2$ etc.) by oxidative addition to form products containing a new

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* For part XXXII. see ref. 1. This work is part of the thesis of B. Klingert [2].

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M—E bond. The highest reactivity is found for the bis(trimethylphosphine) compounds $C_5H_5Co(PMe_3)_2$ [4,5] and $C_5H_5Rh(PMe_3)_2$ [6], but the mixed ligand complexes C_5H_5MLL' with L = PMe_3 and L' = CO [7], CNR [8], C_2H_4 [9] and C_2R_2 [10], in which the metal is less basic, also react, e.g. with Brönsted acids or with methyl iodide, by electrophilic attack at the metal.

To see whether the basicity of the metal atom in the half-sandwiches C_5H_5MLL' is comparable with that of a tertiary phosphorus atom in a phosphine, we decided to examine corresponding tetramethyldiphosphine complexes in which one PMe_2 group is coordinated to the metal and one remains uncoordinated. In this paper we describe the preparation of $C_5Me_5Rh(CO)PMe_3$ and $C_5Me_5Rh(CO)P_2Me_4$ and the reactions of these complexes with some electrophiles.

Results and discussion

The parent dicarbonyl $C_5Me_5Rh(CO)_2$ (I) was first prepared by Kang and Maitlis [11] by the reaction of carbon monoxide with $[C_5Me_5RhCl_2]_2$ in methanol in the presence of zinc. Following our most recent work on the synthesis of pentamethylcyclopentadienyl-metal complexes by use of LiC_5Me_5 [12] and TlC_5Me_5 [13], we found that I can also be obtained from the well-known $[(CO)_2RhCl]_2$ and LiC_5Me_5 in reasonable yields. The corresponding cyclopentadienyl complex $C_5H_5Rh(CO)_2$ is accessible by the same route [14].

$$[(CO)_2RhCl]_2 + 2\,LiC_5Me_5 \rightarrow 2\,\underset{(I)}{C_5Me_5Rh(CO)_2} + 2\,LiCl \qquad (1)$$

Whereas CO displacement reactions of $C_5H_5Rh(CO)_2$ yielding $C_5H_5Rh(CO)L$ (L = PR_3, $P(OR)_3$, CNR etc.) have already been studied in detail [15], no substitution product of the pentamethylcyclopentadienyl complex I has been described. We found that the dicarbonyl reacts with PMe_3 in boiling benzene to form the monosubstituted product in high yields.

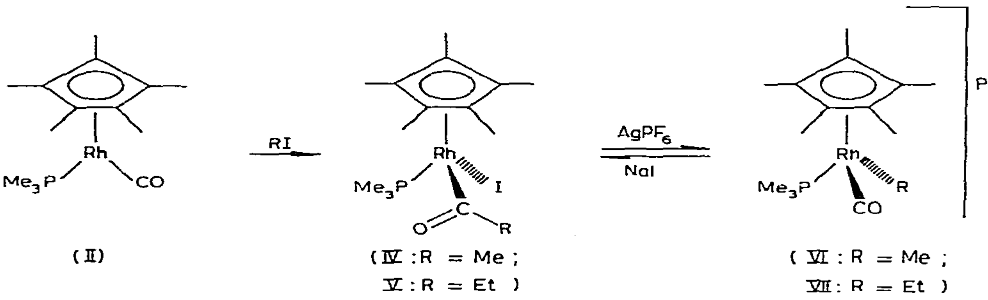
$$I + PMe_3 \rightarrow \underset{(II)}{C_5Me_5Rh(CO)PMe_3} + CO \qquad (2)$$

The shift to lower wave numbers of the CO stretching frequency of II compared with that of $C_5H_5Rh(CO)PMe_3$ [16] indicates an increased electron density at the metal atom in the permethylated complex. In accordance with this, a stable hydrido cation $[C_5Me_5RhH(CO)PMe_3]^+$ is obtained by reaction of II with strong acids such as HBF_4 or CF_3SO_3H. The corresponding PF_6 salt IIIc, which is isolated in presence of NH_4PF_6, reacts smoothly with NaH to re-form the neutral complex II.

$$II \xrightarrow{HX} \underset{\substack{(IIIa:\ X = BF_4;\\ IIIb:\ X = CF_3SO_3)}}{[C_5Me_5RhH(CO)PMe_3]X} \xrightarrow{PF_6^-} \underset{(IIIc)}{[C_5Me_5RhH(CO)PMe_3]PF_6} \qquad (3)$$

The reactivity of II towards methyl and ethyl iodide is very similar to that of the cyclopentadienyl complex $C_5H_5Rh(CO)PMe_3$ [16]. An excess of RI (R = Me, Et) gives the acylrhodium(III) compounds IV and V, which undergo rapid reactions with $AgPF_6$ to yield the hexafluorophosphates of the cationic alkyl

SCHEME 1

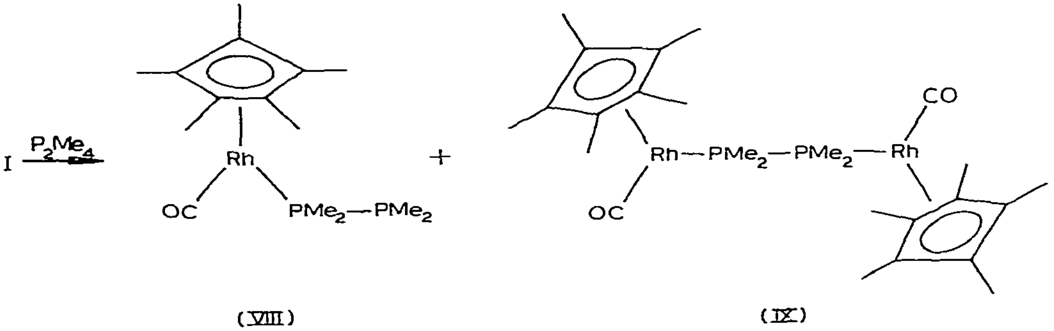


(4)

carbonyl complexes $[C_5Me_5RhR(CO)PMe_3]^+$ (VI and VII) (see Scheme 1). Treatment of VI with NaH gives a mixture of products in which the carbonyl II predominates. It should be mentioned in this context that reaction of $[C_5H_5RhMe(CO)PMe_3]PF_6$ with NaH yields $C_5H_5Rh(CO)PMe_3$ almost quantitatively, whereas the corresponding reaction of $[C_5H_5CoMe(CO)PMe_3]PF_6$ with NaH gives the cobaltdimethyl compound $C_5H_5CoMe_2(PMe_3)$ (15%) and the carbonyl $C_5H_5Co(CO)PMe_3$ (85%) [16].

The ^1H NMR data of the pentamethylcyclopentadienylrhodium complexes containing PMe_3 as ligand are summarized in Table 1.

The tetramethyldiphosphine complex $C_5Me_5Rh(CO)P_2Me_4$ (VIII) can be obtained in 90% yield under similar conditions to those used in the preparation of II, the molar ratio of I : P_2Me_4 being 1 : 1.3. Small amounts of the dinuclear compound $[C_5Me_5Rh(CO)]_2(\mu\text{-}P_2Me_4)$ (IX) are formed as a by-product.



(5)

Complex VIII forms orange crystals which decompose at room temperature even under N_2 but can be stored at —78° C for weeks. The structure is based on elemental analysis, the mass spectrum, and especially the ^1H and ^{31}P NMR data, which confirm the presence of two different PMe_2 groups in the molecule.

In contrast to the trimethylphosphine complex II in which only the metal atom is a center of Lewis basicity, the tetramethyldiphosphine complex VIII can react with an electrophile E either by attack of E at the metal or at the uncoordinated phosphorus atom.

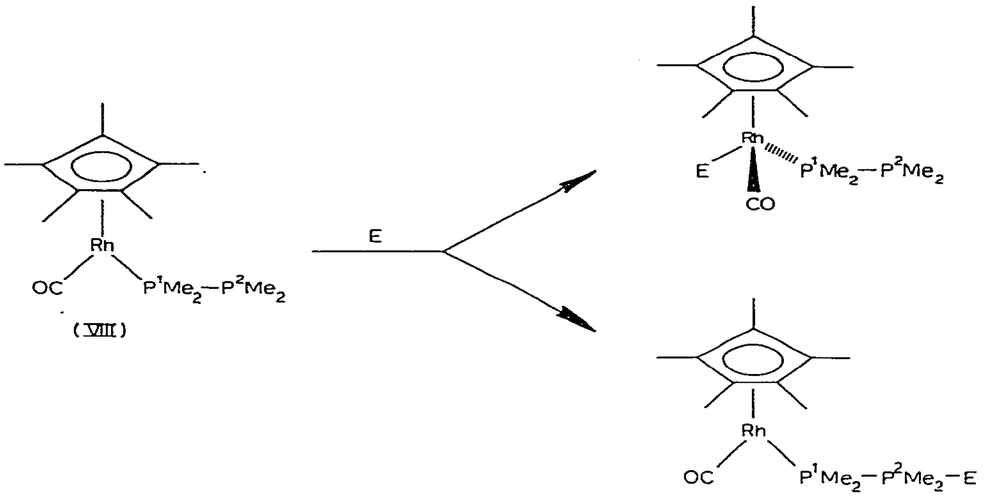
Treatment of VIII with MeI in exactly equivalent amounts in benzene gives the uncharged acetyl complex X as the only product, whereas with an excess of

TABLE 1

^{1}H NMR DATA OF COMPLEXES II—VII (δ in ppm, internal TMS; J in Hz)

Complex	Solvent	δ(C_5Me_5)	J(PH)	J(RhH)	δ(PMe_3)	J(PH)	J(RhH)	δ(COR)	δ(RhR)	J(PH)	J(RhH)
II	C_6H_6	2.15 dd	1.9	0.5	1.23 dd	9.0	1.3				
IIIc	CD_3NO_2	2.15 ddd ^{a}	3.0	0.4	1.75 dd	11.5	1.1		−10.45 dd	30.0	22.5
IV	C_6H_6	1.75 dd	2.7	0.5	1.45 dd	10.3	1.0	3.25 d ^{b}			
V	C_6H_6	1.75 dd	2.8	0.6	1.40 dd	10.3	1.0	3.4 m 2.3 t ^{c}			
VI	CD_3NO_2	2.0 dd	3.0	0.4	1.75 dd	11.0	1.0		0.65 dd	5.6	2.1
VII	CD_3NO_2	2.0 dd	3.1	0.4	1.75 dd	10.8	1.0		^{d}		

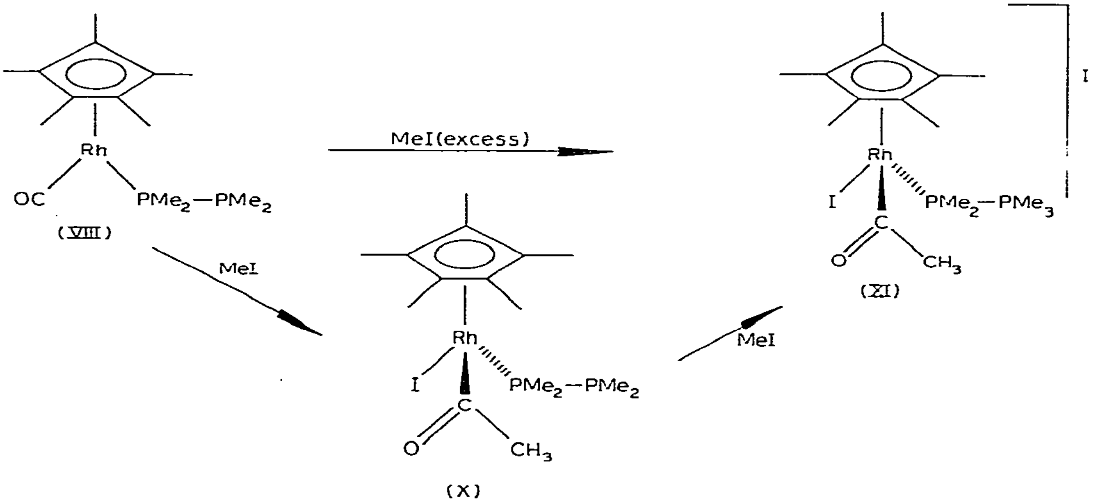
[a] J(HH) 1.4 Hz. [b] J(PH) 0.8 Hz. [c] J(HH) 7.2 Hz. [d] Signals of C_2H_5 protons partly hidden by the doublet of doublets of PMe_3 protons.



(6)

methyl iodide, the salt XI is obtained. XI is also formed by further reaction of X with MeI according to Scheme 2.

SCHEME 2

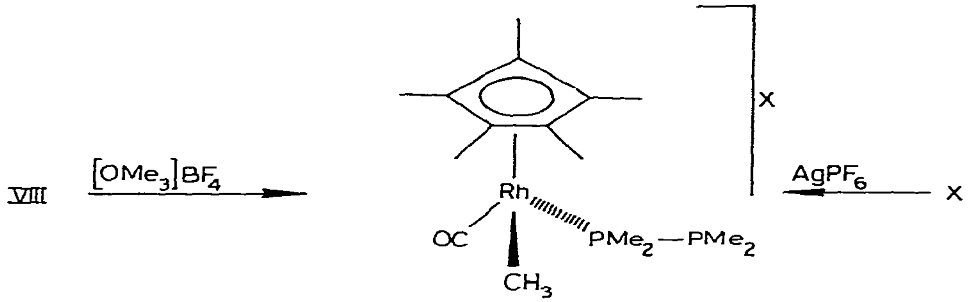


It seems most reasonable to assume that the formation of X occurs by initial attack of methyl iodide at the metal and subsequent migration of the methyl group to the CO ligand. This mechanistic proposal is strongly supported by the reaction of VIII with $[Me_3O]BF_4$ which gives the carbonyl methylrhodium(III) complex XIIa.

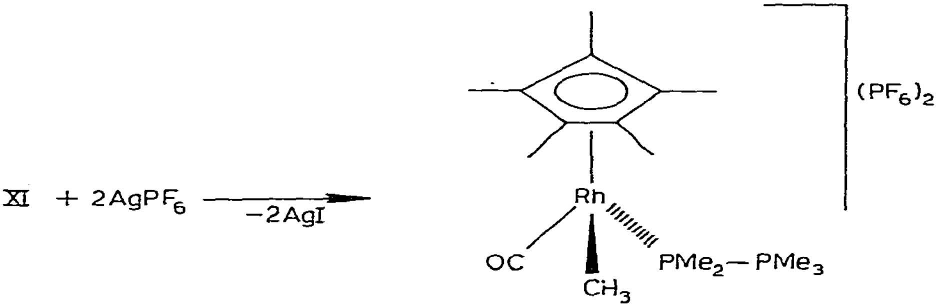
The corresponding PF_6 salt XIIb is more conveniently prepared by reaction of X with $AgPF_6$, the method previously used for the trimethylphosphine compounds VI and VII.

The cationic acetyl complex XI also reacts with $AgPF_6$ to form the hexafluorophosphate of the dication $[C_5Me_5RhMe(CO)P_2Me_5]^{2+}$ (XIII).

Under mass spectrometric conditions, the iodide salt XI looses trimethyl-



(XIIa : X = BF4 ;
XIIb : X = PF6) (7)



(XIII) (8)

phosphine to yield $C_5Me_5RhI(COMe)PMe_2I$. Various attempts to obtain this unknown chiral complex by thermolysis of XI were unsuccessful. It is interesting to note that in the mass spectra of all the acyl iodo complexes IV, V and X is the ion $C_5Me_5RhI^+$ appears with highest intensity. The further fragmentation to form $C_5Me_4CH_2Rh^+$ points to the previously unrecognized stability of tetramethylfulvene metal compounds, examples of which were recently synthesized in our laboratory by proton abstraction from cationic pentamethylcyclopentadienyl metal complexes [13].

The ^1H and ^{31}P NMR data of the pentamethylcyclopentadienylrhodium compounds containing P_2Me_4 and $P_2Me_5^+$ as ligands are summarized in Table 2 and 3.

The dinuclear complex IX formed in small amounts (~5%) in the reaction of I with P_2Me_4, is obtained in 70% yield according to eq. 9.

$$[C_5Me_5Rh]_2(\mu\text{-}CO)_2 + P_2Me_4 \rightarrow IX \qquad (9)$$

Complex IX reacts slowly with an excess of P_2Me_4 to produce VIII. Although the ion from $[C_5Me_5RhPMe_2]_2$ is the most intense fragment in the mass spectrum of IX, we did not succeed in preparing this dinuclear complex by prolonged heating or photolysis of IX. The corresponding cobalt compound $[C_5H_5Co]_2(\mu\text{-}PMe_2)_2$, which has recently been isolated in our laboratory, also behaves as a Lewis base and reacts with acids HX by protonation of the metal—metal bond [17].

TABLE 2

^{1}H NMR DATA OF COMPLEXES VIII—XIII (δ in ppm, int. TMS; *J* in Hz)

Complex	Solvent	δ(C_5Me_5)	*J*(PH)	*J*(RhH)	δ(P^1Me_2)	*J*(PH)	*J*(RhH)	δ(P^2Me_2)	*J*(PH)	δ(COMe)	*J*(PH)	δ(RhMe)
VIII	C_6H_6	2.20 dd	1.8	0.5	1.40 ddd	7.0; 7.8	1.4	1.10 dd	13.8; 4.0			
IX	$CDCl_3$	2.10 dt	[a]	0.5	1.60 m [b]			1.60 m [b]				
X	C_6H_6	1.85 dd	2.6	0.6	1.55 m			1.15 dd [c]	11.8; 4.8	3.30	0.75	
								1.20 dd [c]	12.2; 4.8			
XI	$(CD_3)_2SO$	1.65 d	3.2		2.14 dd [d]	13.6; 3.8				2.80	0.7	
XIIb	CD_3NO_2	2.03 d	2.9		1.50 m [e]							0.75 dd
XIII	CD_3NO_2	2.10 d	3.6		2.25 dd [d]	12.9; 5.3						0.95 dd

Complex	Solvent	*J*(PH)	*J*(RhH)
VIII	C_6H_6		
IX	$CDCl_3$		
X	C_6H_6		
XI	$(CD_3)_2SO$		
XIIb	CD_3NO_2	5.4	2.2
XIII	CD_3NO_2	7.5	2.1

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[a] $|J(P^1H) + J(P^2H)| = 1.0$. [b] Symmetrical multiplet of 8 lines; after ^{31}P-decoupling doublet, *J*(RhH) = 1.3. [c] Diastereotopic methyl groups. [d] Signal corresponds to 15 H. [e] Signal corresponds to 12 H.

TABLE 3

^{31}P NMR DATA OF COMPLEXES VIII—XIII (δ in ppm, ext. 85% H_3PO_4; J in Hz)

Complex	Solvent	$\delta(P^1)$	J(RhP)	J(PP)	$\delta(P^2)$	J(RhP)	$\delta(PF_6)$	J(PF)
VIII	C_6D_6	3.23 dd	187.57	208.41	−55.72 dd	2.98		
IX	$CDCl_3$	18.89 [a]			18.89 [a]			
X	C_6D_6	−10.78 dd	162.26	284.34	−59.72 dd	7.44		
XI	$(CD_3)_2SO$	10.07 dd	173.43	142.91	25.45 dd	5.96		
XIIb	CD_3NO_2	−3.38 dd	122.81	291.78	−57.52 d		−145.51 sept	707.12
XIII	CD_3NO_2	1.26 dd	142.91	125.05	27.38 dd	4.47	−145.51 sept	707.12

[a] Spectrum of XAA′X′-type; $|J(RhP) + J(RhP')| = 188.97$ Hz.

Conclusions

The question whether in a d^8 complex of the general type $C_5R_5M(L)P_2Me_4$ either the metal or the free phosphorus atom of the diphosphine ligand is more basic, has (at least in the case of the pentamethylcyclopentadienylrhodium complex VIII) been answered clearly in favour of the metal. Methylating agents such as MeI or $[OMe_3]BF_4$ when used in a 1 : 1 molar ratio react with VIII by attack at the metal and formation of a methylrhodium cation. Therefore, it seems that the decrease in metal basicity in going from the bis(phosphine) compounds $C_5R_5M(PR'_3)_2$ to the mixed half-sandwiches $C_5R_5M(L)PR'_3$ where L is CO, CNR, C_2H_4 etc., is not large enough to allow preferred attack of the electrophile at the ligand when PR'_3 is P_2Me_4. The course of the reactions of C_5Me_5-$Rh(CO)P_2Me_4$ (VIII) with other electrophiles, in particular with Lewis acidic metal complexes, is apparently being investigated in our laboratory.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 457, mass spectra (MS) on a Varian MAT CH 7, and NMR spectra on the following instruments: Varian T 60 (^{1}H), Varian XL 100 (^{1}H, ^{31}P-decoupled), Bruker WH 90-FT (^{31}P). The starting materials $[(C_2H_4)_2RhCl]_2$ [18], LiC_5Me_5 [19], $[C_5Me_5RhCO]_2$ [20], PMe_3 [21] and P_2Me_4 [22] were prepared by published methods. All reactions were carried out under purified nitrogen.

Preparation of $C_5Me_5Rh(CO)_2$ (I)

$[(C_2H_4)_2RhCl]_2$ (1.0 g, 2.57 mmol) was suspended in 30 ml THF and CO was bubbled through the solution for 3 h. The mixture was filtered and LiC_5Me_5 (781 mg, 5.5 mmol) was added to the filtrate. The solution was stirred for 2 h, then filtered and the solvent was removed. The oily residue was extracted with pentane and the filtered solution was concentrated in vacuo. After sublimation of the dark solid at 10^{-3} Torr and 45° C, red crystals were obtained. Their IR and ^{1}H NMR spectra were identical to those reported in ref. 11. Yield: 200 mg (27%).

Preparation of $C_5Me_5Rh(CO)PMe_3$ (II)

$C_5Me_5Rh(CO)_2$ (1.56 g, 5.32 mmol) was dissolved in 15 ml of C_6H_6 and PMe_3 (610 mg, 8.0 mmol) was added. The solution was stirred for 4 h at 80°C and the solvent and excess phosphine were removed in vacuo. The residue was dissolved in 20 ml pentane and the filtered solution concentrated in vacuo. After cooling to —78°C, orange-red crystals were formed. Yield: 1.69 g (93%). M.p. 90°C. (Found: C, 49.00; H, 7.14; Rh, 30.27. $C_{14}H_{24}OPRh$ calcd.: C, 49.14; H, 7.07; Rh, 30.07%). IR (C_6H_6): ν(CO) 1910 cm^{-1}.

MS (70 eV): *m/e* (I_r) 342 (48; M^+), 314 (100; $M^+ - CO$), 238 (44; $C_5Me_5Rh^+$), 103 (26; Rh^+).

Preparation of $[C_5Me_5RhH(CO)PMe_3]X$ (IIIa—IIIc)

a) $X = BF_4$ (IIIa). A solution of $C_5Me_5Rh(CO)PMe_3$ (211 mg; 0.62 mmol) in 10 ml of ether was treated dropwise with vigorous stirring with a solution of HBF_4 in propionic anhydride and ether (ratio 1 : 4 : 10). The resulting pale brown precipitate was filtered off, washed with ether and pentane, and dried in vacuo. The IR and ^1H NMR spectra of the compound were identical to those of IIIc. Yield: 206 mg (77%).

b) $X = CF_3SO_3$ (IIIb). A solution of $C_5Me_5Rh(CO)PMe_3$ (237 mg; 0.69 mmol) in 20 ml of ether was treated dropwise with a solution of CF_3SO_3H in ether (ratio 1 : 10). The grey precipitate formed was separated from the solution, washed with ether and pentane, and dried in vacuo. Yield: 294 mg (86%).

c) $X = PF_6$ (IIIc). $[C_5Me_5RhH(CO)PMe_3]CF_3SO_3$ (400 mg; 0.81 mmol) was dissolved in 2 ml methanol and 3 ml of a saturated solution of NH_4PF_6 in methanol was added. After stirring for 10 min, the resulting colourless crystals were filtered off, washed with methanol, ether and pentane and dried in vacuo. Yield: 150 mg (38%). (Found: C, 33.97; H, 5.41; Rh, 20.85. $C_{14}H_{25}F_6OP_2Rh$ calcd.: C, 34.44; H, 5.16; Rh, 21.08%). IR (CD_3NO_2): ν(CO) 2065 cm^{-1}. Conductivity (CH_3NO_2): $\Lambda = 97.7$ cm^2 Ω^{-1} mol^{-1}.

Reaction of $[C_5Me_5RhH(CO)PMe_3]BF_4$ with NaH

$[C_5Me_5RhH(CO)PMe_3]BF_4$ (100 mg, 0.23 mmol) was dissolved in 3 ml THF and NaH (30 mg, 1.2 mmol) was added. After stirring for 1 h, the solvent was removed in vacuo. The residue was extracted with pentane and the filtered solution concentrated in vacuo. After cooling to —78°C, orange-red crystals were formed, and proved to be $C_5Me_5Rh(CO)PMe_3$ (II).

Preparation of $C_5Me_5RhCOMe(PMe_3)I$ (IV)

A solution of $C_5Me_5Rh(CO)PMe_3$ (737 mg, 2.15 mmol) in 15 ml of C_6H_6 was treated dropwise with MeI (497 mg, 3.5 mmol). After stirring for 2 h at room temperature, the solvent and excess methyl iodide were removed in vacuo. The residue was dissolved in 10 ml of ether and the filtered solution concentrated in vacuo. After cooling to —78°C, red-brown air-stable crystals were obtained. Yield: 934 mg (90%). M.p. 174°C. (Found: C, 37.06; H, 5.72; Rh, 21.21. $C_{15}H_{27}IOPRh$ calcd.: C, 37.19; H, 5.62; Rh, 21.28%). IR (C_6H_6): ν(CO) 1635 cm^{-1}.

MS (70 eV): *m/e* (I_r) 484 (6; M^+), 469 (1; $M^+ - CH_3$), 456 (5; $M^+ - CO$), 441 (86; $M^+ - COCH_3$), 365 (100; $C_5Me_5RhI^+$), 237 (23; $C_5Me_4CH_2Rh^+$), 103 (3; Rh^+).

Preparation of $C_5Me_5RhCOEt(PMe_3)I$ (V)

The complex was prepared from $C_5Me_5Rh(CO)PMe_3$ and EtI as for the acetyl analogue IV. Dark red air-stable crystals. Yield: 741 mg (75%). M.p. 189°C. (Found: C, 38.95; H, 5.87; Rh, 20.99. $C_{16}H_{29}IOPRh$ calcd.: C, 38.58; H, 5.87; Rh, 20.66%). IR (C_6H_6): ν(CO) 1635 cm^{-1}.

MS (70 eV): m/e (I_r) 498 (4; M^+), 469 (11; $M^+ - C_2H_5$), 441 (69; $M^+ - CO$-C_2H_5), 365 (100; $C_5Me_5RhI^+$), 314 (5; $C_5Me_5RhPMe_3{}^+$), 237 (47; $C_5Me_4CH_2$-Rh^+).

Preparation of $[C_5Me_5RhCH_3(CO)PMe_3]PF_6$ (VI)

$C_5Me_5RhCOMe(PMe_3)I$ (418 mg; 0.86 mmol) was dissolved in 10 ml nitromethane and $AgPF_6$ (253 mg; 1.0 mmol) was added. After stirring for 15 min at room temperature, the mixture was filtered and the filtrate concentrated in vacuo. Ether was added to the concentrated filtrate until a precipitate began to form. The solution was cooled at —20°C to give pale-yellow air-stable crystals which were recrystallized from nitromethane/ether. Yield: 374 mg (87%). (Found: C, 35.65; H, 5.62; Rh, 20.62. $C_{15}H_{27}F_6OP_2Rh$ calcd.: C, 35.86; H, 5.38; Rh, 20.52%). IR (CD_3NO_2): ν(CO) 2060 cm^{-1}. Conductivity (CH_3NO_2): $\Lambda = 85$ cm^2 Ω^{-1} mol^{-1}.

Preparation of $[C_5Me_5RhC_2H_5(CO)PMe_3]PF_6$ (VII)

This was prepared from $C_5Me_5RhCOEt(PMe_3)I$ and $AgPF_6$ as for the methyl analogue VI, using acetone instead of nitromethane as solvent and acetone/ether for the recrystallization. Yield: 261 mg (79%). (Found: C, 36.30; H, 5.94; Rh, 19.86. $C_{16}H_{29}F_6OP_2Rh$ calcd.: C, 37.23; H, 5.66; Rh, 19.94%). IR (CD_3NO_2): ν(CO) 2060 cm^{-1}. Conductivity (CH_3NO_2): $\Lambda = 93.1$ cm^2 Ω^{-1} mol^{-1}.

Reaction of $[C_5Me_5RhCH_3(CO)PMe_3]PF_6$ with NaI

$[C_5Me_5RhCH_3(CO)PMe_3]PF_6$ (50 mg; 0.1 mmol) was dissolved in 2 ml of nitromethane and a few crystals of NaI were added. The solution was stirred for 15 min at 40°C and the remaining solid centrifuged. The NMR spectrum of the solution showed $C_5Me_5RhCOMe(PMe_3)I$ (IV) to be the only reaction product.

Preparation of $C_5Me_5Rh(CO)P_2Me_4$ (VIII)

$C_5Me_5Rh(CO)_2$ (441 mg; 1.5 mmol) was dissolved in 10 ml of C_6H_6 and P_2Me_4 (244 mg; 2.0 mmol) was added dropwise. The clear red solution was stirred for 5 h at 80°C, and the solvent removed. The residue was extracted with pentane (20 ml) and the mixture filtered. (Small amounts of the binuclear complex IX, which is nearly insoluble in pentane, were thus removed.) The concentrated filtrate (~5 ml) was cooled at —78°C and the orange plates separated from the solution. They were recrystallized from pentane and dried in vacuo. Yield: 518 mg (89%). M.p. 78°C. (Found: C, 46.45; H, 7.23; Rh, 26.04. $C_{15}H_{27}OP_2Rh$ calcd.: C, 46.41; H, 7.01; Rh, 26.55%). IR (C_6H_6): ν(CO) 1920 cm^{-1}.

MS (70 eV): m/e (I_r) 388 (18; M^+), 360 (100; $M^+ - CO$), 238 (50; C_5Me_5-Rh^+), 103 (14; Rh^+).

Preparation of $C_5Me_5RhCOMe(P_2Me_4)I$ (X)

$C_5Me_5Rh(CO)P_2Me_4$ (653 mg; 1.68 mmol) was dissolved in 8 ml of C_6H_6 and MeI (293 mg; 1.68 mmol) was added dropwise. The solution was stirred for 2 h, and the solvent was removed. The residue was extracted with ether (20 ml), and the filtered solution was concentrated in vacuo. After cooling at —78° C, dark red crystals were obtained, and these were washed with pentane and dried in vacuo. Yield: 678 mg (76%). M.p. 134°C. (Found: C, 36.18; H, 5.98; Rh, 19.16. $C_{16}H_{30}IOP_2Rh$ calcd.: C, 36.26; H, 5.71; Rh, 19.41%). IR (C_6H_6): ν(CO) 1630 cm^{-1}.

MS (70 eV): m/e (I_r) 530 (5; M^+), 487 (17; M^+ — $COCH_3$), 469 (3; $C_5Me_5RhI(CO)PMe_3^+$), 441 (4; $C_5Me_5RhI(PMe_3)^+$), 427 (17; $C_5Me_5RhI(PMe_2H)^+$), 365 (100; $C_5Me_5RhI^+$), 237 (88; $C_5Me_4CH_2Rh^+$).

Preparation of $[C_5Me_5RhCOMe(P_2Me_5)I]I$ (XI)

$C_5Me_5Rh(CO)P_2Me_4$ (679 mg; 1.75 mmol) was dissolved in 15 ml of C_6H_6 and MeI (710 mg; 5.0 mmol) was added. After a few minutes, a dark red precipitate was formed. The mixture was stirred for 2 h, and the solvent and excess of MeI were removed in vacuo. The residue was dissolved in a small amount of boiling methanol, the hot solution was filtered, and the filtrate concentrated in vacuo. After cooling to room temperature, ether was slowly added until a precipitate began to form. The red air-stable crystals were collected, washed with ether and pentane and dried in vacuo. Yield: 312 mg (27%). M.p. 166°C. (Found: C, 30.52; H, 5.25; Rh, 15.15. $C_{17}H_{33}I_2OP_2Rh$ calcd.: C, 30.38; H, 4.95; Rh, 15.31%). IR (CD_3NO_2): ν(CO) 1625 cm^{-1}. Conductivity (CH_3NO_2): $\Lambda = 84.9\ cm^2\ \Omega^{-1}\ mol^{-1}$.

MS (70 eV): m/e (I_r) 596 (11; $C_5Me_5RhCOMe(PMe_2I)I^+$), 568 (5; $C_5Me_5RhMe(PMe_2I)I^+$), 553 (67; $C_5Me_5Rh(PMe_2I)I^+$), 492 (29; $C_5Me_5RhI_2^+$), 441 (100; $C_5Me_5Rh(PMe_3)I^+$), 426 (12; $C_5Me_5RhPMe_2I^+$).

Complex XI was also prepared from $C_5Me_5RhCOMe(P_2Me_4)I$ and a five-fold excess of MeI in benzene. The procedure for isolating the product was the same as that described above.

Preparation of $[C_5Me_5RhCH_3(CO)P_2Me_4]BF_4$ (XIIa)

$C_5Me_5Rh(CO)P_2Me_4$ (50 mg; 0.13 mmol) was stirred with an equimolar amount of $[OMe_3]BF_4$ in 5 ml of nitromethane for 2 h. The mixture was filtered and the solvent removed in vacuo. The oily residue was dissolved in 2 ml of CD_3NO_2. The ^1H NMR spectrum of the solution showed signals identical to those from XIIb.

Preparation of $[C_5Me_5RhCH_3(CO)P_2Me_4]PF_6$ (XIIb)

$C_5Me_5RhCOMe(P_2Me_4)I$ (283 mg; 0.53 mmol) was dissolved in 10 ml of acetone and a solution of $AgPF_6$ (135 mg; 0.53 mmol) in 5 ml of acetone was added dropwise. After stirring for 15 min, the mixture was filtered and the concentrated filtrate (~2 ml) was added dropwise to ether (20 ml) with vigorous stirring. The resulting precipitate was repeatedly recrystallized from acetone/ether to give bright yellow crystals. Yield: 261 mg (90%). (Found: C, 34.79; H, 5.46; Rh, 18.84. $C_{16}H_{30}F_6OP_3Rh$ calcd.: C, 35.05; H, 5.52; Rh, 18.77%). IR (CD_3NO_2): ν(CO) 2060 cm^{-1}. Conductivity (CH_3NO_2): $\Lambda = 97.4\ cm^2\ \Omega^{-1}\ mol^{-1}$.

Preparation of $[C_5Me_5RhCH_3(CO)P_2Me_5](PF_6)_2$ (XIII)

$[C_5Me_5RhCOMe(P_2Me_5)I]I$ (135 mg; 0.2 mmol) was suspended in 10 ml of acetone and $AgPF_6$ (114 mg; 0.45 mmol) was added. After stirring for 15 min, the mixture was filtered. To the concentrated filtrate ether was slowly added until a precipitate began to form. The pale yellow air-stable crystals were collected, washed with ether and pentane and dried in vacuo. Yield: 113 mg (80%). (Found: C, 28.90; H, 4.86; Rh, 14.14. $C_{17}H_{33}F_{12}OP_4Rh$ calcd.: C, 28.83; H, 4.70; Rh, 14.53%). IR (CD_3NO_2): ν(CO) 2075 cm^{-1}. Conductivity (CH_3NO_2): $\Lambda = 209$ $cm^2\ \Omega^{-1}\ mol^{-1}$.

Preparation of $[C_5Me_5Rh(CO)]_2(\mu\text{-}P_2Me_4)$ (IX)

$[C_5Me_5RhCO]_2$ (520 mg; 0.98 mmol) was dissolved in 10 ml of C_6H_6 and P_2Me_4 (130 mg; 1.07 mmol) was added. The solution was stirred for 2 h at 60°C and the solvent was removed. The residue was suspended in 15 ml of pentane and the mixture was filtered. The remaining solid was washed with pentane and dried in vacuo. After recrystallization from ether orange air-stable crystals were obtained. Yield: 444 mg (69%). M.p. 178°C. (Found: C, 46.86; H, 6.47; Rh, 30.66. $C_{26}H_{42}O_2P_2Rh_2$ calcd.: C, 47.72; H, 6.47; Rh, 31.45%). IR (C_6H_6): ν(CO) 1920 cm^{-1}.

MS (70 eV): m/e (I_r) 654 (1; M^+), 626 (1; $M^+ - CO$), 598 (100; $M^+ - 2\ CO$), 583 (77; $M^+ - 2\ CO - CH_3$), 373 (22; $(C_5Me_5)_2Rh^+$), 238 (37; $C_5Me_5Rh^+$).

Complex IX was also obtained as a by-product (yield ~5%) in the reaction of $C_5Me_5Rh(CO)_2$ with P_2Me_4 (see preparation of VIII).

Reaction of $[C_5Me_5Rh(CO)]_2(\mu\text{-}P_2Me_4)$ with P_2Me_4

A solution of $[C_5Me_5Rh(CO)]_2(\mu\text{-}P_2Me_4)$ (50 mg; 0.077 mmol) and an excess of P_2Me_4 (~0.5 mmol) in 3 ml C_6H_6 was stirred for 16 d at 100°C. The solvent was then removed and the remaining residue extracted with pentane (2 ml). The concentrated filtrate was cooled at —78°C and a few orange crystals collected. The ^1H NMR spectrum (in C_6D_6) of the product was identical to that of an authentic sample of $C_5Me_5Rh(CO)P_2Me_4$ (VIII).

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