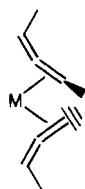with the spectroscopic data is

The major problem lies in the steric interaction of the α-methyl groups with the rings. This Zr(II) structure pulls the methyl groups much further into the wedge than required for the metallocyclic possibility. Also, we have been unable to displace allenes from these molecules by further reaction with allenes,

acetylene, or CO_2. This seems as well to suggest the likelyhood of a very stable Zr(IV) metallocyclic structure.

In a later paper we will show that the bis(allene) adduct is in fact an intermediate in the thermal rearrangment of II.

Registry No. I, 75125-14-3; II, 75112-05-9; [$(C_5Me_5)_2ZrN_2]_2N_2$, 54387-50-7; allene, 463-49-0; 1,3-dimethylallene, 28383-16-6.

Contribution from the Research School of Chemistry,
The Australian National University, Canberra, A.C.T., 2600, Australia

Oxidative Addition of Acyl Chlorides to Chlorotris(dimethylphenylphosphine) Complexes of Rhodium(I) and Iridium(I). Crystal and Molecular Structure of [RhCl(COCH₃)(PMe₂Ph)₃]PF₆, an Acetyl Complex Which Undergoes Unusually Fast Methyl Migration in Solution

M. A. BENNETT,* J. C. JEFFERY, and G. B. ROBERTSON

Acyl chlorides RCOCl react with MClL₃ (M = Rh, Ir; L = PMe₂Ph) to give six-coordinate acyl–rhodium(III) or –iridium(III) complexes MCl₂(COR)L₃ (M = Ir, R = CH₃ (1), CH₂CH₂CH₃ (2), CH(CH₃)₂ (3); M = Rh, R = CH₃ (4), CH₂CH₃ (5), CH(CH₃)₂ (6)). Treatment of 1 and 2 with NH₄PF₆ generates six-coordinate alkylcarbonyl salts [IrClR(CO)L₃]PF₆ (R = CH₃ (7), CH₂CH₂CH₃ (8)) as a result of alkyl group migration, whereas 3 fails to react. Similar treatment of the rhodium complex 4 in the absence of oxygen gives [RhCl(COCH₃)L₃]PF₆ (9), which is shown by three-dimensional X-ray structural analysis to contain an approximately square-pyramidal cation with an apical acetyl group. Crystals of 9 are monoclinic, of space group $P2_1/c$, with a = 12.685 (2) Å, b = 15.209 (3) Å, c = 16.552 (2) Å, β = 95.96 (1)°, and Z = 4. The structure was solved by conventional Patterson and difference Fourier syntheses and refined by full-matrix least-squares methods to a conventional R factor of 0.044 (4949 reflections). Important bond lengths are Rh–C(acyl) = 1.971 (5) Å, Rh–Cl = 2.391 (1) Å, Rh–P(trans to Cl) = 2.285 (1) Å, Rh–P(trans to L) = 2.389 (4) Å, and C(acyl)–O = 1.184 (6) Å. A nonbonded interaction between the acetyl methyl group and the chlorine ligand shifts the latter from an ideal equatorial site toward the vacant apical position. In solution, 9 is in equilibrium with a six-coordinate methylcarbonylrhodium(III) complex [RhCl(CH₃)(CO)L₃]PF₆ (10) analogous to 7. Methyl migration occurs at an intermediate rate on the ¹H and ³¹P NMR time scales at room temperature but is slow at –70 °C, where the ratio of 9 to 10 is ca. 2:1. Possible reasons for this behavior are (1) the structure of 9 in the solid state may be close to that of the transition state for methyl migration and (2) the positive charge on the metal atom may help to destabilize the ground states of 9 and 10 relative to the transition state by reducing π bonding to the acyl and CO groups, respectively.

Introduction

Acyl chlorides RCOCl oxidatively add to the planar d⁸ complexes MCl(CO)L₂ (M = Rh, Ir; L = various tertiary phosphines and arsines) to give six-coordinate acyl–metal(III) complexes MCl₂(COR)(CO)L₂.¹⁻⁴ The corresponding additions to IrCl(N₂)(PPh₃)₂⁴ or to MClL₃ (L = PPh₃, M = Rh, Ir; L = PMePh₂, M = Ir)⁴⁻¹¹ give initially five-coordinate

Scheme I
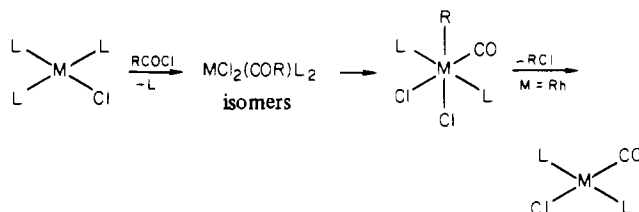
acyl–metal(III) complexes MCl₂(COR)L₂ which subsequently isomerize by alkyl group migration to form six-coordinate alkyl–metal(III) complexes MCl₂R(CO)L₂ (Scheme I). In the case of rhodium, ready elimination of RCl (or olefin and HCl) gives RhCl(CO)L₂ as the final product. An interesting

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Table I. Analytical and IR Data for Acyls and Alkyls of Iridium(III) and Rhodium(III)^a

	% calcd			% found			ν(C=O) or ν(C≡O)	ν(M–Cl)
	C	H	Cl	C	H	Cl		
IrCl$_2$(COCH$_3$)(PMe$_2$Ph)$_3$ (1)	43.3	5.0		43.1	5.0		1610	270
IrCl$_2$(COCH$_2$CH$_2$CH$_3$)(PMe$_2$Ph)$_3$ (2)	44.9	5.4		45.1	5.4		1605	270
IrCl$_2$[COCH(CH$_3$)$_2$](PMe$_2$Ph)$_3$ (3)	44.9	5.4		44.6	5.5		1610	275
RhCl$_2$(COCH$_3$)(PMe$_2$Ph)$_3$ (4)	49.5	5.8	11.2	48.7	5.7	11.4	1640	310, 260, 230
RhCl$_2$(COCH$_2$CH$_3$)(PMe$_2$Ph)$_3$ (5)	50.3	5.9	11.0	50.2	5.8	10.95	1635	310, 280, 240
RhCl$_2$[COCH(CH$_3$)$_2$](PMe$_2$Ph)$_3$ (6)	51.0	6.1	10.8	51.7	6.1	10.6	1635	310, 270, 250
[IrCl(CH$_3$)(CO)(PMe$_2$Ph)$_3$]PF$_6$ (7)	37.6	4.4		37.7	4.3		2050	310
[IrCl(CH$_2$CH$_2$CH$_3$)(CO)(PMe$_2$Ph)$_3$]PF$_6$ (8)	39.2	4.7		39.4	4.6		2020	315
[RhCl(COCH$_3$)(PMe$_2$Ph)$_3$]PF$_6$ (9)	42.2	4.9	4.8	42.5	5.2	4.9	1720^b	295, 260, 230^c

^{a} IR data (cm^{-1}) refer to Nujol mulls. ^{b} 1715 cm^{-1} (ν(C=O)), 2050 cm^{-1} (ν(C≡O)) in CH$_2$Cl$_2$. ^{c} Not established whether all three bands are due to ν(Rh–Cl).

Table II. ^{1}H and ^{31}P NMR Data^a

	phosphine methyls (J_{PH})^b		other alkyl protons	δ_P (J_{RhP})	J_{PP}'^{c}
	cis	trans			
IrCl$_2$(COCH$_3$)(PMe$_2$Ph)$_3$ (1)	1.40 (11)	1.83, 1.88 (9)	2.24 (s, 3, COCH$_3$)	−36.5, −40.0	19
IrCl$_2$(COCH$_2$CH$_2$CH$_3$)(PMe$_2$Ph)$_3$ (2)	1.40 (11)	1.82, 1.90 (9)	0.70 (t, 3, CH$_3$, J = 7 Hz), 1.30 (m, 2, CH$_2$CH_2CH$_3$), 2.52 (t, 3, CH_2CH$_2$CH$_3$, J = 7 Hz)	−36.6, −38.9	19
IrCl$_2$[COCH(CH$_3$)$_2$](PMe$_2$Ph)$_3$ (3)	1.40 (11)	1.90, 1.96 (8)	0.58 (d, 6, CH$_3$, J = 6 Hz), 3.56 (m, 1, CH)	d	d
RhCl$_2$(COCH$_3$)(PMe$_2$Ph)$_3$ (4)	1.30 (10)	1.87, 1.93 (8)	2.37 (s, 3, COCH$_3$)	−5.6 (107), +8.0 (158)	26
RhCl$_2$(COC$_2$H$_5$)(PMe$_2$Ph)$_3$ (5)	1.30 (10)	1.84, 1.92 (8)	0.73 (t, 3, CH$_3$, J = 7 Hz), 2.83 (q, 2, CH$_2$)	−5.7 (106), +8.3 (155)	25
RhCl$_2$[COCH(CH$_3$)$_2$](PMe$_2$Ph)$_3$ (6)	1.32 (10)	1.94, 2.01 (8)	0.61 (d, 6, CH$_3$, J = 7 Hz), 3.69 (m, 1, CH)	−6.4 (106), +8.6 (152)	24
[IrCl(CH$_3$)(CO)(PMe$_2$Ph)$_3$]PF$_6$ (7)	1.47 (10)	1.82, 1.96 (9)	0.89 (~1:3:3:1 q, 3, IrCH$_3$, $J_{HP(cis)}$ ≈ $J_{HP(trans)}$ ≈ 5–6 Hz)	−38.4, −44.5	14
[IrCl(CH$_2$CH$_2$CH$_3$)(CO)(PMe$_2$Ph)$_3$]PF$_6$ (8)	1.60 (9)	1.83, 1.87 (8)	0.1 (m, 3, CH$_3$), 1.26 (br m, 6, CH$_2$CH$_2$)	−35.1, −49.3	13
[RhCl(COCH$_3$)(PMe$_2$Ph)$_3$]PF$_6$ (9)^e	1.09 (10)	1.70, 1.93	3.13 (s, 3, COCH$_3$)	+1.3 (103), +17.1 (153)	24
[RhCl(CH$_3$)(CO)(PMe$_2$Ph)$_3$]PF$_6$ (10)^e	1.27 (10)	1.81, 1.98	~0.86 (br m, RhCH$_3$)^f	−4.1 (83), −18.6 (68)	21

^{a} Except where stated, ^{1}H NMR spectra were measured in CDCl$_3$ at 34 °C with (CH$_3$)$_4$Si (δ = 0) as internal reference; coupling constants (J) are in Hz. Except where stated, ^{31}P{^{1}H} NMR spectra were measured in CDCl$_3$ at 32 °C; chemical shifts (δ_P) downfield of external 85% H$_3$PO$_4$ are taken as positive; coupling constants (J) are accurate to ±1 Hz. ^{b} For trans PMe$_2$Ph ligands "J_{PH}" refers to separation between outer lines of the 1:2:1 triplet ($^2J_{PH}$ + $^4J_{PH}$). ^{c} Coupling constant between cis and equivalent trans ^{31}P nuclei. ^{d} Not measured owing to poor solubility. ^{e} ^{1}H NMR in CD$_2$Cl$_2$ at −60 °C; ^{31}P NMR in CD$_2$Cl$_2$ at −72 °C. ^{f} Tentative assignment.

feature of the addition of α-branched acyl chlorides to IrCl(PPh$_3$)$_3$ or IrCl(PMePh$_2$)$_3$ is the exclusive formation of n-alkyliridium(III) complexes, e.g., IrCl$_2$(CH$_2$CH$_2$CH$_3$)(CO)L$_2$ from (CH$_3$)$_2$CHCOCl, presumably by isomerization of an undetected intermediate *sec*-alkyliridium(III) complex.[10,11] We were interested to know whether processes similar to those mentioned above would occur in complexes containing the smaller, more basic ligand dimethylphenylphosphine, and we report here on the oxidative addition of acyl chlorides to MCl(PMe$_2$Ph)$_3$ (M = Rh, Ir). A brief account has appeared elsewhere.[12]

Experimental Section

Measurement, analytical, and general procedures have been described.[11] The complexes [IrCl(C$_8$H$_{14}$)$_2$]$_2$[13] and [RhCl(C$_2$H$_4$)$_2$]$_2$[14] were prepared by literature methods. Analytical and IR spectroscopic data are given in Table I, and ^{1}H and ^{31}P NMR data are in Table II.

Preparations. Acyldichlorotris(dimethylphenylphosphine)iridium(III) Complexes, IrCl$_2$(COR)(PMe$_2$Ph)$_3$ (R = CH$_3$ (1), CH$_2$CH$_2$CH$_3$ (2), CH(CH$_3$)$_2$ (3)). An excess (ca. 0.1 mL) of the appropriate acyl

chloride was added by syringe to an orange solution containing [IrCl(C$_8$H$_{14}$)$_2$]$_2$ (0.3 g, 0.355 mmol) and dimethylphenylphosphine (0.28 g, 2.01 mmol) in ether (15 mL). The solution rapidly became paler, and a white solid precipitated. After 20 min of stirring and after addition of hexane (ca. 5 mL), the product was collected, washed with three 2-mL portions of hexane, and dried in vacuo. The resulting white microcrystals of 1–3, obtained in ca. 80% yield, were analytically pure but could be recrystallized from dichloromethane/methanol.

Alkylcarbonylchlorotris(dimethylphenylphosphine)iridium(III) Hexafluorophosphate, [IrClR(CO)(PMe$_2$Ph)$_3$]PF$_6$ (R = CH$_3$ (7), CH$_2$CH$_2$CH$_3$ (8)). A solution of IrCl$_2$(COR)(PMe$_2$Ph)$_3$ (0.2 g) in dichloromethane (1 mL) and acetone (10 mL) was treated with a large excess (ca. 0.15 g) of NH$_4$PF$_6$ dissolved in the minimum volume of acetone to produce an immediate turbidity. The white suspension was stirred for 30 min, solvent was removed in vacuo, and the residue was extracted with three 5-mL portions of dichloromethane. The combined extracts were evaporated to dryness, and the gummy white residue was recrystallized from methanol/ether to give colorless needles of 7 (ca. 80% yield) or 8 (ca. 70% yield).

Acyldichlorotris(dimethylphenylphosphine)rhodium(III), RhCl$_2$(COR)(PMe$_2$Ph)$_3$ (R = CH$_3$ (4), C$_2$H$_5$ (5), CH(CH$_3$)$_2$ (6)). Dimethylphenylphosphine (0.64 g, 4.6 mmol) was added to a stirred solution of [RhCl(C$_2$H$_4$)$_2$]$_2$ (0.3 g, 0.77 mmol) in benzene (20 mL). Ethylene was evolved, and the red solution which formed was stirred for ca. 10 min. An excess of the appropriate acyl chloride (ca. 0.25 mL) was added by syringe. The solution became orange-yellow over a period of ca. 5 min and was stirred for 20 min. Occasionally it was necessary to filter at this stage to remove a small amount of fine brown

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precipitate formed by slight decomposition of [RhCl(C₂H₄)₂]₂. The solution was evaporated to ca. 5-mL volume, and crystallization was induced by trituration with a trace of methanol; the process was completed by adding hexane. The resulting pale yellow needles were washed with three 2-mL portions of hexane and were dried in vacuo. Yields of **4–6** were typically 80–90%.

Acetylchlorotris(dimethylphenylphosphine)rhodium(III) Hexafluorophosphate, [RhCl(COCH₃)(PMe₂Ph)₃]PF₆ (9). Rigorous exclusion of oxygen is essential to the success of this preparation. A solution of **4** (0.1 g, 0.16 mmol) in acetone (5 mL) and dichloromethane (2 mL) was treated with a large excess (ca. 0.2 g) of solid NH₄PF₆. The mixture was stirred for 30 min, the solvent was evaporated in vacuo, and the residue was extracted with three 5-mL portions of dichloromethane. The combined extracts were evaporated to dryness, and the gummy yellow residue was dissolved in ca. 2 mL of methanol. Crystallization was induced by scratching and completed by dropwise addition of hexane. The bright yellow crystals were washed with hexane, and after they were dried in vacuo, the yield of **9** was 0.08 g (ca. 70%).

Collection and Reduction of X-ray Intensity Data. Approximate cell dimensions of crystals of **9** were obtained from preliminary Weissenberg [(h0l), (h1l)] and precession [(hk0), (0kl)] photographs. Systematic absences (h0l) for $l = 2n + 1$ and (0k0) for $k = 2n + 1$ were observed, thus uniquely defining the monoclinic space group as $P2_1/c$ (C_{2h}^5, No. 14). For $Z = 4$ there is no imposed crystallographic symmetry.

Reflection data were collected on a Picker FACS-I fully automatic four-circle diffractometer with the crystallographic b/b^* axis and the instrumental ϕ axis approximately coincident. Accurate cell dimensions and crystal orientation matrices were obtained from the least-squares refinement[15] of the 2θ, ω, χ, and Φ values of 12 carefully centered high-angle reflections ($2\theta > 45°$).

Crystal Data for [RhCl(COCH₃)(P(CH₃)₂C₆H₅)₃]PF₆: fw = 740.82, monoclinic, space group $P2_1/c$, $a = 12.685$ (2) Å, $b = 15.209$ (3) Å, $c = 16.552$ (2) Å, $\beta = 95.96$ (1)°, $V_{calcd} = 3175.8$ Å³, $\rho_{calcd} = 1.55$ g cm⁻³, $\rho_{obsd} = 1.53$ (1) g cm⁻³, $Z = 4$, μ(Mo Kα) = 8.46 cm⁻¹, $t = 22 \pm 2$ °C. Crystal dimensions, quoted as the perpendicular distance between faces (hkl): (100 to 1̄00), 0.075 mm; (001 to 001̄), 0.175 mm; (110 to 1̄1̄0), 0.2 mm; (1̄10 to 11̄0), 0.2 mm.

Details of the experimental conditions and data collection methods are in Table III (supplementary material). During data collection the intensities of three "standard" reflections showed a smooth isotropic decrease of ca. 4% which was assumed to be independent of 2θ and the intensity data were corrected accordingly.

Reflection intensities were reduced to values of $|F_o|$, and each reflection was assigned an individual estimated standard deviation ($\sigma(F_o)$).[16] For this data set the instrumental "uncertainty factor" p[17] was assumed to be $0.002^{1/2}$. Reflection data were sorted, equivalent reflections were averaged, and reflections with $I/\sigma(I) < 3.0$ were discarded as being unobserved. Reflections for which the individual background measurements differed by more than 10σ were also discarded. The statistical R factor (R_s) for the 4949 reflections of the terminal data set was 0.031.

Solution and Refinement of the Structure. The structure was solved by conventional Patterson and difference Fourier syntheses and was initially refined by block-diagonal least-squares methods. Both the atomic scattering factors and the anomalous scattering factors for the nonhydrogen atoms were taken from ref 18. Toward the end of the refinement process, the data were corrected for absorption by the literature method.[19] The phenyl hydrogen atoms were located

(15) The programs contained in the Picker Corp FACS-I disk operating system (1972) were used for all phases of diffractometer control and data collection.
(16) The formulas used for data reduction: $Lp = (\cos^2 2\theta + \cos^2 2\theta_m)/2 \cdot \sin 2\theta$, where Lp is the Lorentz–polarization factor and θ and θ_m (6.06°) are the reflection and monochromator Bragg angles, respectively; I (net peak intensity) $= [CT - (t_p/t_b)(B_1 + B_2)]$, where CT is the total peak count in t_p s and B_1 and B_2 are the individual background counts in $t_b/2$ s; $\sigma(I) = [CT + (t_p/t_b)^2(B_1 + B_2)]^{1/2}$; $\sigma(F_o) = \{[\sigma(I)/Lp]^2 + (p|F_o|^2)^2\}^{1/2}/2|F_o|$; $\sigma_s(F_o)$ (the reflection esd from counting statistics alone) $= \sigma(I)/2Lp(|F_o|)$; $R = \sum(|F_o| - |F_c|)/\sum|F_o|$; R_s (the statistical R factor) $= \sum\sigma_s(F_o)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.
(17) Busing, W. R.; Levy, H. A. *J. Chem. Phys.* **1957**, *26*, 563–568. Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197–204.
(18) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99–101, 149–150.

Scheme II

1, M = Ir, R = CH₃
2, M = Ir, R = CH₂CH₂CH₃
3, M = Ir, R = CH(CH₃)₂
4, M = Rh, R = CH₃
5, M = Rh, R = CH₂CH₃
6, M = Rh, R = CH(CH₃)₂

from a difference synthesis and were included in the scattering model as fixed contributions (C–H = 0.95 Å,[20] $B_H = B_C$). The hydrogen atom coordinates and temperature factors were recalculated prior to each cycle of refinement. Eight of the 21 methyl hydrogen atoms were observed in a final difference synthesis, but no attempt was made to include these in the final scattering model.

The six fluorine atoms of the PF₆⁻ anion were readily located but showed evidence of either thermal libration or possibly orientational disorder. It was not possible to resolve individual fluorine atom peaks into separate components, and accordingly the observed spread of fluorine electron density is approximately accounted for by the large anisotropic temperature factors of these atoms. A difference Fourier synthesis in this region showed six residual peaks between 0.5 and 0.8 e Å⁻³, but it was not possible to relate these to a second disordered component of the PF₆⁻ anion.

A final cycle of full-matrix least-squares refinement with all nonhydrogen atoms anisotropic and fixed phenyl hydrogen contributions gave $R = 0.044$ (R_w[16] = 0.054). No individual parameter shift was greater than 0.1 of the corresponding esd. A final difference Fourier synthesis showed no residual peaks greater than 0.5 e Å⁻³ except for those, previously noted, in the vicinity of the PF₆⁻ anion and those attributable to methyl hydrogen atoms. The standard deviation of an observation of unit weight, defined as $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ (where m is the number of observations and n is the number of parameters varied), is 1.55. An examination of $|F_o|$ and $|F_c|$ shows no evidence of serious extinction effects, and there is no serious dependence of the minimized function on either $|F_o|$ or $\lambda^{-1} \sin \theta$.

Final atomic positional and thermal parameters, together with their estimated standard deviations (where appropriate), are listed in Table IV. Final tables of structure factors are available as supplementary material.

Computer Programs. The data reduction (SETUP), sorting (SORTER), Fourier (ANUFOR), least-squares (SFLS), and absorption correction (TOMPAB) programs have been described elsewhere.[21] The figures were produced with the use of ORTEP.[22] All calculations were carried out on the Univac 1108 computer of the Australian National University Computer Services Centre.

Preparative and Spectroscopic Results

The complexes MCl(PMe₂Ph)₃ (M = Rh, Ir), prepared in situ by treatment of the olefin complex [IrCl(C₈H₁₄)₂]₂ or [RhCl(C₂H₄)₂]₂ with 6 mol of dimethylphenylphosphine/mol of dimer,[23,24] react with linear or α-branched acyl halides RCOCl to give pale yellow or colorless, crystalline σ-acyl complexes MCl₂(COR)(PMe₂Ph)₃ (Scheme II). In contrast with the corresponding triphenylphosphine and diphenylmethylphosphine systems, the products are six-coordinate, contain three rather than two phosphine ligands, and do not readily rearrange to σ alkyls. The rhodium(III) acyls **4** and

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(20) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213–1214.
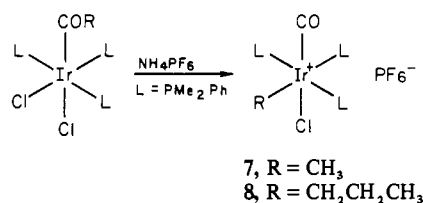(21) Ferguson, J.; Mau, A. W.-H.; Whimp, P. O. *J. Am. Chem. Soc.* **1979**, *101*, 2363–2369.
(22) Johnson, C. K. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, Tenn., 1965.
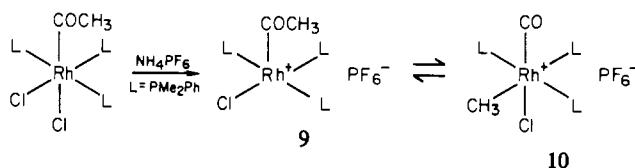(23) Intille, G. M. *Inorg. Chem.* **1972**, *11*, 695–702.
(24) The iridium(I) complex in fact may be five-coordinate IrCl(C₈H₁₄)(PMe₂Ph)₃. Cf. IrCl(C₈H₁₄)(PMe₃)₃: Herskovitz, T.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 1615–1616.

Scheme III

COR ... CO structures ... 7, R = CH₃, 8, R = CH₂CH₂CH₃ shown as:

7, $R = CH_3$
8, $R = CH_2CH_2CH_3$

Scheme IV

$$9 \qquad 10$$

5 have been prepared previously[2] by treatment of RhCl(PPh₃)₃ successively with PMe₂Ph and the appropriate acyl chloride; additional spectral data are given here. The IR spectra of **1–6** show strong bands at 1610–1640 cm⁻¹ (acyl ν(C=O)) and at ca. 270 cm⁻¹ (ν(M–Cl) for Cl trans to PMe₂Ph). The spectra of the rhodium complexes also exhibit weak bands at ca. 230 and 310 cm⁻¹ which could not be clearly located in the spectra of the corresponding iridium complexes. The first band may be due to ν(M—Cl) for Cl trans to acyl. As already noted for **4** and **5**[2] the P–CH₃ ¹H NMR resonance patterns consist of a doublet due to PMe₂Ph trans to Cl and two overlapping 1:2:1 triplets due to the mutually trans PMe₂Ph ligands, each of which has inequivalent methyl groups. The ³¹P{¹H} NMR spectra of the rhodium complexes **4–6** show a first-order AM₂X pattern consisting of a double doublet (trans P) and a double triplet (cis P), the magnitude of J_{RhP} being greater for P trans to Cl than for P trans to P,[25,26] as expected on the basis of relative trans influences.[27] In contrast, the ³¹P{¹H} NMR spectra of the iridium complexes **1** and **2** are not first order and show a seven-line AB₂ pattern which was analyzed and simulated to yield the parameters given in Table II.

It was hoped that treatment of the acyliridium(III) complexes with NH₄PF₆ would generate a vacant coordination site and allow alkyl migration to take place. Indeed, **1** and **2** react with NH₄PF₆ at room temperature to give six-coordinate alkylcarbonyliridium(III) salts [IrClR(CO)(PMe₂Ph)₃]PF₆ **7** and **8** (Scheme III). The 2-methylpropanoyl complex **3** does not react with NH₄PF₆ under the same conditions. The IR spectra of complexes **7** and **8** show a strong terminal ν(CO) band at ca. 2050 cm⁻¹ and a ν(Ir–Cl) band at ca. 310 cm⁻¹ characteristic of Cl trans to CO in octahedral iridium(III) complexes.[28,29] The phosphine ligands in **7** and **8** give rise to ¹H and ³¹P NMR spectra generally similar to those of the precursors **1** and **2** except that the ³¹P resonances appear as a typical first-order (AX₂) pattern. The Ir–CH₃ ¹H NMR resonance pattern in **7** is a 1:3:3:1 quartet, which is consistent with the proposed stereochemistry if J_{HP}(cis) ≈ J_{HP}(trans) ≈ 5–6 Hz.

Under strictly anaerobic conditions the acetylrhodium(III) complex **4** reacts with NH₄PF₆ to give a bright yellow salt [RhCl(COCH₃)(PMe₂Ph)₃]PF₆ **(9)** the cation of which has been shown by X-ray crystallography (see below) to be square pyramidal with the acetyl group in the apical position. In the

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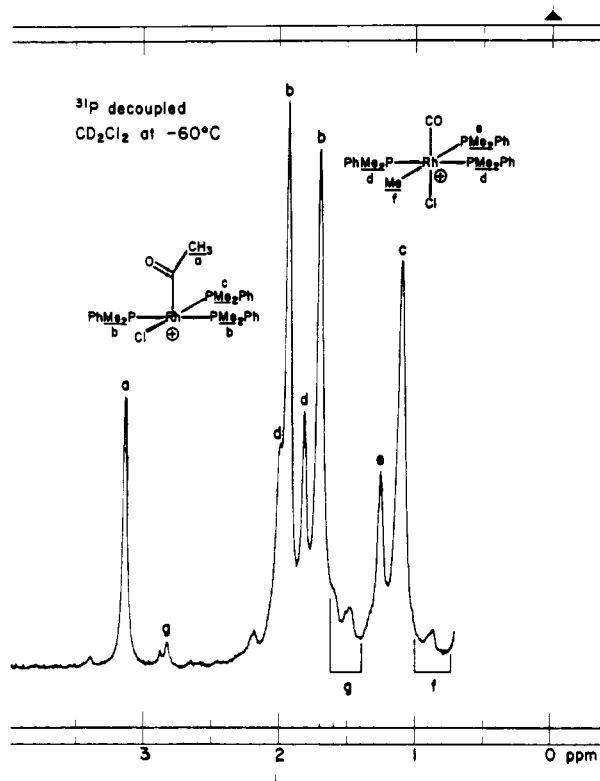
Figure 1. ¹H{³¹P} NMR spectrum of an equilibrium mixture of [RhCl(COCH₃)(PMe₂Ph)₃]PF₆ **(9)** and [RhCl(CH₃)(CO)(PMe₂Ph)₃]PF₆ **(10)** in CD₂Cl₂ at –60 °C. Peaks labeled g are presumed to be impurity resonances.
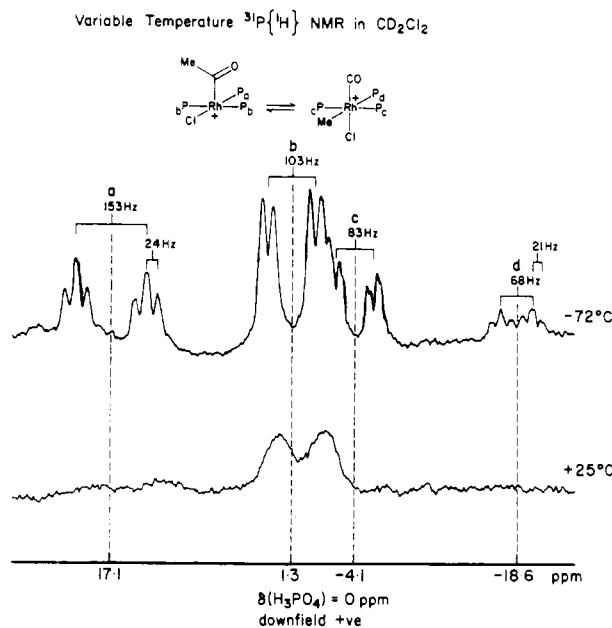
Figure 2. ³¹P{¹H} NMR spectrum of an equilibrium mixture of **9** and **10** at 25 and –72 °C. Peaks labeled g are presumed to be impurity resonances.

solid-state IR spectrum of **9** there is a strong acyl ν(C=O) band at 1720 cm⁻¹, ca. 60 cm⁻¹ higher frequency than ν(C=O) for the six-coordinate precursor **4**. In dichloromethane solution there is an additional ν(CO) band at 2050 cm⁻¹ which we assign to a six-coordinate methylcarbonylrhodium(III) species **10** analogous to the iridium(III) complex **7** (Scheme IV). An interesting feature of the equilibrium between **9** and **10** is that methyl migration occurs at an intermediate rate on the NMR time scale at room temperature. The ¹H{³¹P} NMR spectrum

Table IV. Final Atomic Positional and Thermal Parameters for [RhCl(COCH₃)(P(CH₃)₂C₆H₅)₃]PF₆[a]

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Rh	0.17754 (3)	0.79393 (2)	0.25925 (2)	C(6)	0.4024 (5)	0.9345 (4)	0.3252 (4)
P(1)	0.00493 (10)	0.73698 (9)	0.21798 (9)	C(11)	−0.0919 (4)	0.8030 (3)	0.1563 (3)
P(2)	0.18642 (10)	0.87012 (9)	0.14120 (8)	C(12)	−0.1296 (4)	0.8775 (4)	0.1896 (4)
P(3)	0.35618 (10)	0.82105 (8)	0.31326 (8)	C(13)	−0.2001 (4)	0.9327 (4)	0.1444 (4)
Cl	0.18687 (12)	0.66744 (9)	0.34543 (9)	C(14)	−0.2310 (5)	0.9128 (5)	0.0658 (5)
P(4)	0.25113 (14)	0.44471 (13)	0.06651 (11)	C(15)	−0.1964 (5)	0.8369 (5)	0.0309 (4)
F(1)	0.3038 (6)	0.4640 (4)	0.1552 (3)	C(16)	−0.1265 (4)	0.7805 (4)	0.0762 (4)
F(2)	0.1422 (6)	0.4704 (7)	0.0820 (8)	C(21)	0.3038 (4)	0.9358 (3)	0.1300 (3)
F(3)	0.2256 (9)	0.3520 (4)	0.0911 (5)	C(22)	0.3930 (4)	0.8970 (4)	0.1012 (3)
F(4)	0.2617 (7)	0.5424 (4)	0.0480 (5)	C(23)	0.4819 (5)	0.9473 (5)	0.0950 (4)
F(5)	0.2121 (5)	0.4260 (4)	−0.0251 (3)	C(24)	0.4847 (6)	1.0357 (6)	0.1151 (5)
F(6)	0.3603 (5)	0.4241 (9)	0.0540 (5)	C(25)	0.3976 (6)	1.0733 (4)	0.1412 (4)
C(7)	0.1315 (4)	0.9001 (4)	0.3142 (3)	C(26)	0.3071 (4)	1.0249 (4)	0.1493 (3)
C(8)	0.0960 (5)	0.8794 (4)	0.3976 (4)	C(31)	0.4461 (4)	0.7638 (3)	0.2525 (3)
O	0.1363 (4)	0.9729 (3)	0.2896 (3)	C(32)	0.5493 (4)	0.7937 (4)	0.2480 (4)
C(1)	−0.0719 (5)	0.7079 (5)	0.3022 (4)	C(33)	0.6129 (4)	0.7512 (5)	0.1967 (4)
C(2)	0.0169 (5)	0.6339 (4)	0.1632 (4)	C(34)	0.5746 (5)	0.6797 (4)	0.1502 (4)
C(3)	0.1859 (6)	0.7870 (5)	0.0614 (3)	C(35)	0.4755 (5)	0.6498 (4)	0.1568 (4)
C(4)	0.0818 (4)	0.9480 (5)	0.1036 (4)	C(36)	0.4104 (4)	0.6911 (3)	0.2070 (3)
C(5)	0.3909 (5)	0.7806 (4)	0.4169 (3)				

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	0.00396 (2)	0.00220 (1)	0.00212 (1)	0.00013 (2)	0.00057 (1)	0.00004 (1)
P(1)	0.00450 (8)	0.00273 (6)	0.00349 (6)	−0.00059 (5)	0.00073 (5)	0.00015 (5)
P(2)	0.00449 (8)	0.00352 (6)	0.00226 (5)	−0.00057 (6)	0.00038 (5)	0.00041 (4)
P(3)	0.00449 (8)	0.00292 (6)	0.00244 (5)	0.00012 (5)	0.00001 (5)	−0.00009 (4)
Cl	0.00835 (11)	0.00322 (6)	0.00387 (6)	−0.00010 (7)	0.00040 (7)	0.00117 (5)
P(4)	0.00678 (12)	0.00548 (9)	0.00447 (8)	−0.00044 (8)	−0.00043 (8)	0.00065 (7)
F(1)	0.0298 (9)	0.0115 (4)	0.0059 (3)	0.0000 (5)	−0.0035 (4)	0.0003 (3)
F(2)	0.0149 (7)	0.0216 (9)	0.0316 (12)	0.0019 (6)	0.0102 (8)	−0.0051 (8)
F(3)	0.0485 (16)	0.0079 (4)	0.0118 (5)	−0.0079 (7)	−0.0034 (7)	0.0027 (4)
F(4)	0.0357 (12)	0.0091 (4)	0.0132 (5)	−0.0076 (6)	−0.0122 (6)	0.0048 (4)
F(5)	0.0258 (8)	0.0102 (4)	0.0076 (3)	−0.0003 (5)	−0.0069 (4)	−0.0010 (3)
F(6)	0.0114 (6)	0.0488 (16)	0.0107 (5)	0.0113 (8)	0.0010 (4)	−0.0027 (7)
C(7)	0.0058 (4)	0.0035 (3)	0.0032 (2)	0.0007 (2)	0.0003 (2)	−0.0008 (2)
C(8)	0.0102 (6)	0.0057 (4)	0.0031 (2)	0.0002 (4)	0.0022 (3)	−0.0007 (2)
O	0.0134 (5)	0.0032 (2)	0.0052 (2)	0.0019 (2)	0.0026 (3)	−0.0003 (2)
C(1)	0.0064 (4)	0.0071 (4)	0.0053 (3)	−0.0011 (3)	0.0019 (3)	0.0024 (3)
C(2)	0.0077 (5)	0.0026 (2)	0.0065 (3)	−0.0010 (3)	0.0004 (3)	−0.0010 (2)
C(3)	0.0111 (6)	0.0070 (4)	0.0026 (2)	−0.0037 (4)	0.0012 (3)	−0.0016 (3)
C(4)	0.0047 (4)	0.0064 (4)	0.0062 (3)	0.0001 (3)	−0.0004 (3)	0.0035 (3)
C(5)	0.0074 (4)	0.0062 (4)	0.0024 (2)	0.0001 (3)	−0.0003 (2)	0.0010 (2)
C(6)	0.0076 (4)	0.0028 (2)	0.0044 (3)	−0.0003 (3)	−0.0014 (3)	−0.0010 (2)
C(11)	0.0040 (3)	0.0031 (2)	0.0038 (2)	−0.0009 (2)	0.0003 (2)	0.0002 (2)
C(12)	0.0054 (4)	0.0036 (3)	0.0041 (2)	−0.0011 (2)	0.0010 (2)	−0.0001 (2)
C(13)	0.0052 (4)	0.0042 (3)	0.0060 (3)	0.0002 (3)	0.0012 (3)	0.0006 (3)
C(14)	0.0052 (4)	0.0057 (4)	0.0060 (4)	0.0004 (3)	0.0002 (3)	0.0023 (3)
C(15)	0.0065 (5)	0.0078 (4)	0.0040 (3)	−0.0008 (4)	−0.0005 (3)	0.0007 (3)
C(16)	0.0057 (4)	0.0043 (3)	0.0042 (3)	−0.0005 (3)	0.0002 (2)	−0.0003 (2)
C(21)	0.0048 (3)	0.0041 (3)	0.0021 (2)	−0.0011 (2)	0.0004 (2)	0.0007 (2)
C(22)	0.0062 (4)	0.0048 (3)	0.0031 (2)	−0.0006 (3)	0.0008 (2)	0.0007 (2)
C(23)	0.0060 (4)	0.0084 (5)	0.0053 (3)	−0.0009 (4)	0.0021 (3)	0.0018 (3)
C(24)	0.0087 (4)	0.0076 (5)	0.0059 (4)	−0.0040 (4)	0.0004 (4)	0.0018 (4)
C(25)	0.0108 (6)	0.0038 (3)	0.0045 (3)	−0.0025 (4)	0.0002 (3)	0.0005 (2)
C(26)	0.0062 (4)	0.0040 (3)	0.0035 (2)	−0.0007 (3)	0.0003 (2)	0.0003 (2)
C(31)	0.0046 (3)	0.0029 (2)	0.0030 (2)	0.0003 (2)	0.0006 (2)	0.0003 (2)
C(32)	0.0047 (3)	0.0040 (3)	0.0050 (3)	−0.0002 (3)	0.0005 (2)	0.0003 (2)
C(33)	0.0047 (4)	0.0058 (3)	0.0062 (3)	0.0003 (3)	0.0019 (3)	0.0006 (3)
C(34)	0.0080 (5)	0.0050 (3)	0.0052 (3)	0.0013 (3)	0.0028 (3)	0.0001 (3)
C(35)	0.0070 (4)	0.0037 (3)	0.0048 (3)	0.0007 (3)	0.0013 (3)	−0.0009 (2)
C(36)	0.0050 (3)	0.0031 (3)	0.0037 (2)	0.0000 (2)	0.0002 (2)	0.0000 (2)

[a] Estimated standard deviations are in parentheses.

of **9** in CD_2Cl_2 at 32 °C shows two very broad resonances at ca. δ 1.25 and 1.85 due to the methyl groups of the exchange-averaged cis and trans PMe₂Ph ligands of **9** and **10**. The methyl resonance of the acetyl group of **9** appears as a broad signal at ca. δ 2.6, but the Rh–CH₃ resonance of **10** could not be located, possibly because it is masked by the cis PMe₂Ph resonance at δ 1.25. When the temperature is lowered to −70 °C, methyl migration becomes slow on the NMR time scale and the ¹H{³¹P} NMR spectrum shows fairly sharp signals which are consistent with an approximately 2:1 mixture of **9** and **10** (Figure 1 and Table II). The ³¹P{¹H} NMR spectrum

at −72 °C (Figure 2) shows two sets of AB₂X (close to AM₂X) resonances, the relative intensities of which are also consistent with a 2:1 mixture of **9** and **10**. For both species, J_{RhP} for P trans to Cl is greater than that for P trans to P, and in **9** the mutually trans ³¹P nuclei resonate at lower field than the ³¹P nucleus trans to Cl, as is observed in **4–6** and in other octahedral rhodium(III) complexes. The value of 68 Hz for J_{Rh-P} trans to CH₃ in **10** appears reasonable by comparison with the value of 83 Hz for the mutually trans ³¹P nuclei in the same complex, given the higher trans influence of CH₃ relative to tertiary phosphines.[27] It is also noteworthy that the ratio of
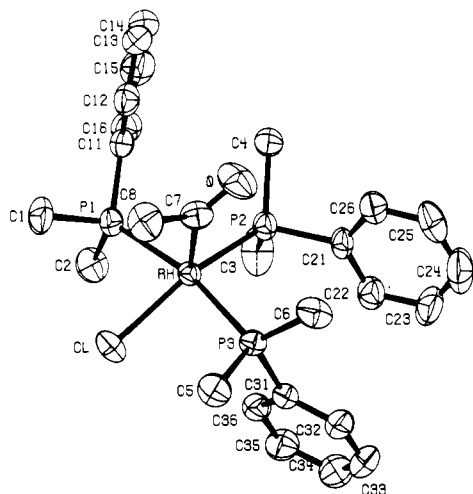
Figure 3. Overall stereochemistry of the [RhCl(COCH₃)(PMe₂Ph)₃]⁺ cation, together with the atom numbering scheme.

the J_{RhP} values for P trans to P in **9** and **10** is close to $^5/_6$, as expected on the basis of the s characters of the dsp³- and d²sp³-hybrid metal orbitals presumably employed in **9** and **10**, respectively. When the solution is warmed to −25 °C and then to +25 °C, the equilibrium shifts in favor of the acyl **9** and concomitantly the pairs of cis and trans ³¹P resonances broaden and collapse toward their respective coalescence points. Although the variable-temperature ³¹P NMR data might be explicable in terms of an intramolecular exchange of phosphine ligands in the five-coordinate structure **9**, such a process cannot account for the behavior of the acetyl methyl resonance in the ¹H NMR spectrum. In view of the complexity of the ³¹P spectra and of the variation of equilibrium constant with temperature, we have not yet attempted to carry out line shape analysis and extract rate data.

There was no spectroscopic evidence for the presence of five-coordinate acyls in equilibrium with the iridium(III) complexes **7** and **8**.

Description of the Structure of 9

The crystal structure consists of discrete [RhCl-(COCH₃)(PMe₂Ph)₃] cations and PF₆ anions separated by normal van der Waals distances. A perspective view of the molecule is shown in Figure 3 which also gives the atom labeling scheme. Hydrogen atom nomenclature follows that of the parent carbon atoms. Principal bond distances and angles are listed in Table V and the results of mean-plane calculations are in Table VI.

The coordination about the rhodium atom is approximately square pyramidal with the acetyl group occupying the apical coordination site. The sixth site is occupied by one of the ortho hydrogen atoms, H(36), from phenyl ring 3 (Rh–H(36) = 2.98 Å, C(7)–Rh–H(36) = 153°). The five-coordinate cation can be derived from the six-coordinate precursor **4** by loss of chloride ion trans to the acetyl group, a ligand known to have a high trans influence. Square-pyramidal geometry has also been reported for RhCl₂(COCH₂CH₂Ph)(PPh₃)₂,[7] RhCl₂-(COPh)(Ph₂PCH₂CH₂CH₂PPh₂),[30] [Ph₄As][RhI-(COC₂H₅)(PPh₃)(mnt)],[31] and Rh(COCH₂CH₂CH₃)-(PEt₃)₂(mnt)[32] (mnt = maleonitriledithiolate, [C₂(CN)₂S₂]²⁻), and this appears to be the preferred arrangement for five-coordinate complexes of d⁶ metal ions.[33] The only exception

Table V. Principal Bond Distances and Interbond Angles[a]

(a) Bond Distances (Å)

Rh–P(1)	2.388 (1)	P(3)–C(5)	1.833 (5)
Rh–P(2)	2.285 (1)	P(3)–C(6)	1.827 (5)
Rh–P(3)	2.384 (1)	P(1)–C(11)	1.816 (5)
Rh–Cl	2.391 (1)	P(2)–C(21)	1.818 (5)
Rh–C(7)	1.971 (5)	P(3)–C(31)	1.819 (5)
C(7)–C(8)	1.528 (8)	P(4)–F(1)	1.575 (6)
C(7)–O	1.184 (6)	P(4)–F(2)	1.484 (7)
P(1)–C(1)	1.837 (6)	P(4)–F(3)	1.512 (6)
P(1)–C(2)	1.826 (6)	P(4)–F(4)	1.526 (6)
P(2)–C(3)	1.828 (6)	P(4)–F(5)	1.572 (5)
P(2)–C(4)	1.839 (6)	P(4)–F(6)	1.456 (6)

(b) Interbond Angles (Deg)

P(1)–Rh–P(3)	167.90 (5)	C(1)–P(1)–C(2)	104.4 (3)
P(2)–Rh–Cl	156.17 (5)	C(1)–P(1)–C(11)	100.3 (3)
P(1)–Rh–P(2)	93.70 (5)	C(2)–P(1)–C(11)	106.4 (3)
P(1)–Rh–Cl	82.29 (5)	Rh–P(2)–C(3)	105.7 (2)
P(3)–Rh–P(2)	95.95 (5)	Rh–P(2)–C(4)	121.2 (2)
P(3)–Rh–Cl	85.94 (5)	Rh–P(2)–C(21)	118.7 (2)
P(1)–Rh–C(7)	97.0 (2)	C(3)–P(2)–C(4)	104.6 (3)
P(2)–Rh–C(7)	91.3 (2)	C(3)–P(2)–C(21)	104.3 (3)
P(3)–Rh–C(7)	90.1 (2)	C(4)–P(2)–C(21)	100.5 (3)
Cl–Rh–C(7)	112.5 (2)	Rh–P(3)–C(5)	114.8 (2)
Rh–C(7)–C(8)	112.2 (4)	Rh–P(3)–C(6)	119.1 (2)
Rh–C(7)–O	125.5 (4)	Rh–P(3)–C(31)	109.6 (2)
O–C(7)–C(8)	122.2 (5)	C(5)–P(3)–C(6)	99.9 (3)
Rh–P(1)–C(1)	114.4 (2)	C(5)–P(3)–C(31)	104.7 (3)
Rh–P(1)–C(2)	109.4 (2)	C(6)–P(3)–C(31)	107.4 (3)
Rh–P(1)–C(11)	120.5 (2)		

(c) Nonbonded Distances (Å)

Cl–C(5)	3.23	Cl–C(3)[b]	3.64
Cl–C(1)	3.34	O–C(4)	3.11
Cl–C(2)	3.56	C(8)–C(1)	3.63
Cl–C(8)	3.56		

[a] Estimated standard deviations are in parentheses. [b] Atom belongs to a symmetry-related molecule.

Table VI. Mean-Plane Calculations[a]

plane	equation	atom	dist, Å	atom	dist, Å
1	0.4222X − 0.6934Y −	P(1)	−0.190	Cl	0.200
	0.5839Z + 9.8088 = 0	P(2)	0.171	Rh*	−0.293
		P(3)	−0.181		
2	−0.8929X − 0.1105Y −	Rh	−0.007	C(7)	0.027
	0.4365Z + 4.8038 = 0	O	−0.012	C(8)	−0.008
3	−0.9319X − 0.2145Y −	Rh	−0.018	C(7)	0.004
	0.2923Z + 5.5030 = 0	P(2)	0.007	P(1)*	2.341
		Cl	0.007	P(3)*	−2.392
4	0.1760X + 0.4705Y −	Rh	0.132	C(7)	−0.01
	0.8647Z − 2.1765 = 0	P(1)	−0.061	P(2)*	2.413
		P(3)	−0.061	Cl*	−2.001

planes[b]	angle, deg	planes	angle, deg	planes	angle, deg
1–2	87.4	1–4	75.4	2–4	80.3
1–3	85.7	2–3	10.4	3–4	89.3

[a] The equations of the planes $AX + BY + CZ + D = 0$ are referenced to an orthogonal coordinate system and were calculated by an eigenvector/eigenvalue method. $X = 12.685x - 1.719z$; $Y = 15.209y$; $Z = 16.462z$; (x, y, z) are the fractional coordinates. Atoms with asterisks were not included in the mean-plane calculations. [b] The angles between the mean planes are given as the acute angle between their normals.

is RhCl₂(COCH₂Ph)(PPh₃)₂, which is stated[34] to be trigonal bipyramidal with apical phosphine ligands, though in view of the reported Cl–Rh–Cl angle of 54° this report must be considered suspect.

There are marked distortions from ideal square-pyramidal geometry in the present structure. The P(1)–Rh–P(3) angle

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$(167.90\ (5)°)$ is ca. 12° larger than the P(2)–Rh–Cl angle $(156.17\ (5)°)$, and the acyl carbon C(7)–Rh–Cl angle $(112.5\ (2)°)$ is ca. 20° greater than the average C(7)–Rh–P(n) angle $(92.8°$ for $n = 1$–3). The acyl plane C(7)–C(8)–O–Rh is inclined by only 10.4° to the coordination plane P(2)–Rh–Cl–C(7), resulting in significant nonbonded contacts between the acyl group and the trans-equatorial phosphorus and chlorine ligands. The short contact between Cl and the acyl methyl group C(8) (3.63 Å; cf. 3.8 Å for the sum of the van der Waals radii) prevents the chlorine atom from occupying an ideal equatorial position and causes it to shift toward the vacant apical site. This movement is constrained within the plane Rh–P(2)–C(7) so as to minimize nonbonded contacts with the adjacent phosphorus atoms P(1) and P(3), thus accounting for the unexpectedly large C(7)–Rh–Cl angle mentioned above. Similar though somewhat smaller distortions are observed in [RhCl(NO)(Ph₂PCH₂CH₂CH₂P(Ph)CH₂CH₂CH₂PPh₂)]PF₆[35] and in RhCl₂(COPh)-(Ph₂PCH₂CH₂CH₂PPh₂).[30] The average Rh–P–C angle for the substituents lying above the basal coordination plane is ca. 12° larger than that found for substituents lying below it, which may reflect a tendency for substituents to fill the vacant coordination site, thereby relieving steric congestion in the molecule.

The Rh–C distance in **9** of 1.971 (5) Å is at the lower end of the range found in related rhodium(III) acyl complexes, e.g., Ph₄As[RhI(COC₂H₅)(PPh₃)(mnt)] (2.006 (14) Å),[31] Rh(COCH₂CH₂CH₃)(PEt₃)₂(mnt) (2.001 (7) Å),[32] RhCl₂-(COPh)(Ph₂PCH₂CH₂CH₂PPh₂) (1.991 (3) Å),[30] RhCl₂-(COCH₂CH₂Ph)(PPh₃)₂ (1.93 (7) Å),[34] [Me₃PhN]₂[Rh₂I₆-(COCH₃)₂(CO)₂] (2.062 (23) Å),[36] and [Rh₂Cl₃(COCH₃)₂-(PMe₂Ph)₄]PF₆ (average 2.002 (4) Å).[37] Even if allowance is made for the difference in covalent radii between sp²- and sp³-hybridized carbon atoms (ca. 0.01–0.02 Å), the Rh–C-(acyl) distances are still significantly shorter than the range of 2.05–2.09 Å obtained from a tabulation of Rh–C(methyl) distances.[38] A particularly close comparison can be drawn with the apical Rh–C(methyl) distance of 2.081 (10) Å observed in the square-pyramidal complex RhI₂(CH₃)-(PPh₃)₂·C₆H₆.[39] The acetyl group in **9** is planar within experimental error, and the C(7)–C(8) and C(7)–O distances of 1.528 (8) and 1.184 (6) Å are normal. The Rh–P bond lengths to the mutually trans PMe₂Ph ligands (2.384 (1) and 2.388 (1) Å) are longer than the Rh–P distance to the PMe₂Ph ligands trans to Cl (2.285 (1) Å), in accord with the relative positions of tertiary phosphines and Cl⁻ in the trans-influence series. The latter distance and the Rh–Cl bond length trans to PMe₂Ph (2.391 (1) Å) are similar to the corresponding distances in the square-pyramidal complexes [RhCl(NO)-(Ph₂PCH₂CH₂CH₂P(Ph)CH₂CH₂CH₂PPh₂)]PF₆ (2.282 (4) Å, Rh–P; 2.408 (4) Å, Rh–Cl)[35] and [RhCl(N₂Ph)-(Ph₂PCH₂CH₂CH₂P(Ph)CH₂CH₂CH₂PPh₂)]PF₆ (2.274 (3) Å, Rh–P; 2.403 (2) Å, Rh–Cl).[40] In contrast, the average Rh–P distance to the mutually trans PMe₂Ph ligands in **9** (2.386 Å) is significantly greater than the range observed for the corresponding Rh–P distances in these two complexes (2.352 (2)–2.374 (3) Å), presumably as a consequence of the presence of a chelating phosphine.

Discussion

Oxidative addition of acyl chlorides to MCl(PMe₂Ph)₃ (M = Rh, Ir) cannot be used to prepare alkylmetal(III) complexes MCl₂R(CO)(PMe₂Ph)₂. The acyl complexes MCl₂(COR)-(PMe₂Ph)₃, unlike their PPh₃- or PMePh₂-containing counterparts, do not readily provide a vacant coordination site by dissociation of tertiary phosphine, so that the alkyl group cannot migrate. When R is a straight-chain alkyl group, a vacant site can be created by the NH₄PF₆-induced loss of one chloride ion, probably that trans to the acyl group; this allows the alkyl group to migrate. In the case of iridium(III), the equilibrium between the resulting five-coordinate acyl [MCl(COR)(PMe₂Ph)₃]⁺ and the six-coordinate alkyl [MClR(CO)(PMe₂Ph)₃]⁺ is entirely on the side of the alkyl, whereas in the case of rhodium(III) both species are present in solution in ca. 2:1 ratio at –70 °C, and only the acyl can be detected in the solid state. These observations reflect the well-known preference of rhodium(III) relative to iridium(III) to adopt five- rather than six-coordination. At present we cannot explain why similar cations cannot be generated by treatment of MCl₂[COCH(CH₃)₂](PMe₂Ph)₃ with NH₄PF₆.

The factors which control the position and rate of establishment of acyl–alkyl equilibria in rhodium(III) and iridium(III) complexes are not well understood. We have noted previously[11] that equilibrium constants for *cis*-IrCl₂(COR)-(PMePh₂)₂ $\rightleftharpoons$ *cis*-IrCl₂R(CO)(PMePh₂)₂ in dichloromethane are ≥50, 3.2, and 4.5 for R = CH₃, C₂H₅, and n-C₃H₇, respectively; the equilibria are established within the time required to prepare the solutions but are not rapid on the NMR time scale. In contrast, the acyls *trans*-IrCl₂(COR)(PPh₃)₂ isomerize slowly but completely to *trans*-IrCl₂R(CO)(PPh₃)₂.[8,9] If, as suggested previously,[11] this difference in behavior can be ascribed to destabilization of the six-coordinate alkyl by steric repulsion between the cis PMePh₂ ligands, then the failure to observe an acyl in solutions of the tris(dimethylphenylphosphine) complexes [IrCl(COR)(PMe₂Ph)₃]⁺ is perhaps surprising.

The acyl–alkyl equilibrium between **9** and **10** is believed to provide the first example of a methyl group which migrates rapidly on the NMR time scale at room temperature. The equilibrium

$$\textit{trans-}RhCl_2(COCH_3)(PPh_3)_2 \rightleftharpoons$$
$$\textit{trans-}RhCl_2(CH_3)(CO)(PPh_3)_2$$
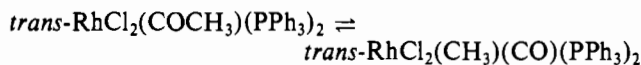
for which $K_{eq} \simeq 0.29$ at 298 K, may fall into a similar category, since the ³¹P resonances for these two species are reported[7] to diverge by ca. 0.6 ppm at 258 K. It was suggested that this was due to presence of a small amount of an isomer or isomers, but an alternative explanation could be that the system is not at the slow-exchange limit at 298 K.

In the present case, the rates of migration of the methyl group in both directions must be of the order of 10^2–10^3 s⁻¹ at ambient temperature and thus are ca. 10^7–10^8 times greater than the rate constants k_1 for the forward reaction in the equilibrium[41,42]

$$RMn(CO)_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RCOMn(CO)_4$$
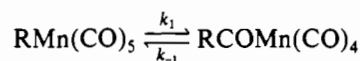
We suggest that methyl migration from carbon to rhodium in **9** takes place via a concerted movement of the chlorine atom to the vacant apical site of the square pyramid and of the methyl group to the vacated equatorial site (**11**). The facts that the apical acetyl group is in nonbonded contact with the equatorial chlorine atom and that the chlorine atom itself lies

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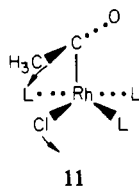
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significantly closer to the vacant site than expected for ideal square-pyramidal geometry may account in part for the rapidity of the migration; i.e., the structure of the acetyl complex may be close to that of the transition state for methyl migration even though this would require concerted reorientation of the substituents on phosphorus. Another important contributor to the fast methyl migration may be the positive charge on the complex. On the basis of calculations on model systems, it has been suggested[43] that a strong π-acceptor ligand such as NO placed opposite either CH_3 or CO will lower the ac-

tivation energy for methyl migration from metal to carbonyl carbon whereas a strong σ donor such as a tertiary phosphine will have the reverse effect. In the present case, the effect of the phosphine ligands may be outweighed by that of the positive charge, which reduces π bonding to the CO group of **10** and to the acetyl group of **9** relative to that in uncharged complexes and thus destabilizes the ground states relative to the transition state for methyl migration.

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Supplementary Material Available: Listings of data collection details (Table III), atomic coordinates and isotropic thermal parameters, bond distances and angles, and structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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Formation and X-ray Structure of the Dinuclear Tri-μ-chloro Acetylrhodium(III) Complex [Rh₂Cl₃(COCH₃)₂(PMe₂Ph)₄]PF₆·0.5C₂H₄Cl₂

M. A. BENNETT,* J. C. JEFFERY, and G. B. ROBERTSON

Reaction of RhCl₂(COR)L₃ (L = PMe₂Ph; R = CH₃, C₂H₅) with NH₄PF₆ in the presence of air gives dinuclear tri-μ-chloro acylrhodium(III) complexes [Rh₂Cl₃(COR)₂L₄]PF₆. The acetyl complex has also been made by treating [RhCl(C₂H₄)₂]₂ (1 mol) successively with dimethylphenylphosphine (4 mol), acetyl chloride, and NH₄PF₆. Crystals of [Rh₂Cl₃(COCH₃)₂L₄]PF₆·0.5C₂H₄Cl₂ obtained from dichloromethane/methanol are monoclinic, of space group $P2_1/c$, with a = 11.174 (2) Å, b = 19.340 (4) Å, c = 21.931 (4) Å, β = 106.33 (1)°, and Z = 4. The structure was solved by direct methods using MULTAN and refined by block-diagonal least-squares analysis to a conventional R factor of 0.037 (6104 reflections). The cation has a confacial bioctahedral structure, each rhodium atom being octahedrally coordinated by an acetyl group, two phosphine ligands, and three bridging chlorine atoms. One of the chlorine atoms (Cl(2)) is trans to a phosphine ligand on each rhodium atom; the other two (Cl(1), Cl(3)) are trans to an acetyl group on one rhodium atom and a phosphine ligand on the other. The Rh–Cl distances trans to L show considerable variation, those involving Cl(2) (Rh(1)–Cl(2) = 2.485 (1) Å, Rh(2)–Cl(2) = 2.462 (2) Å) being significantly longer than those involving Cl(1) or Cl(3) (Rh(1)–Cl(1) = 2.431 (2) Å, Rh(2)–Cl(3) = 2.446 (1) Å). All of these are significantly shorter than the Rh–Cl distances trans to acetyl (Rh(1)–Cl(3) = 2.624 (1) Å, Rh(2)–Cl(1) = 2.612 (1) Å), indicating the high trans influence of the acetyl group relative to that of dimethylphenylphosphine. Other important distances are Rh–C(acyl) = 2.002 (4) Å, C(acyl)–O = 1.202 (7) Å (average) and Rh–Rh = 3.3284 (6) Å, the last of these being incompatible with significant metal–metal interaction. An unexpected feature is the presence in the unit cell of two molecules of the anti conformer of 1,2-dichloroethane, the source of which is unknown.

Introduction

In the preceding paper[1] we showed that the complex RhCl₂(COCH₃)L₃ (L = PMe₂Ph),[2] formed by oxidative addition of acetyl chloride to RhClL₃,[1,3] loses chloride ion on treatment with NH₄PF₆. The product isolated in the absence of air, [RhCl(COCH₃)L₃]PF₆, has an essentially square-pyramidal structure with an apical acetyl group in the solid state, but in solution this species is in equilibrium with a six-coordinate methylrhodium(III) salt [RhCl(CH₃)(CO)L₃]PF₆. Solutions of this equilibrium mixture smell strongly of dimethyl-

phenylphosphine, and unless air is rigorously excluded, it is difficult to obtain a pure product having reproducible NMR spectra. We report here a single-crystal X-ray structural characterization of a compound formed when [RhCl(COCH₃)L₃]PF₆ is exposed to air.

Experimental Section

Measurement, analytical, and general procedures have been described.[4] The complexes [RhCl(C₂H₄)₂]₂[5] and RhCl₂(COR)L₃[1,3] (R = CH₃, C₂H₅) were prepared by literature methods.

Preparations. (i) [Rh₂Cl₃(COR)₂L₄]PF₆ (1) (R = CH₃, C₂H₅) from RhCl₂(COR)L₃. To a solution of RhCl₂(COCH₃)L₃ (0.3 g, 0.48 mmol) in dichloromethane (10 mL) and acetone (10 mL) was added ammonium hexafluorophosphate (0.09 g, 0.55 mmol) dissolved in the

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