

LiC_6H_5 , $\text{C}_6\text{H}_5\text{MgBr}$, or $\text{CH}_3\text{C}_6\text{H}_4\text{MgBr}$ under conditions similar to those used for the cobalt clusters. Alkyl Grignards also gave no alkyl derivatives. Instead, in each case extensive decomposition occurred and the only compounds isolated were the starting material and the ether derivative $\text{H}_3\text{Ru}_3(\mu_3\text{-COCH}_3)(\text{CO})_9$ resulting from reaction of $\text{H}_3\text{Ru}_3(\mu_3\text{-CBr})(\text{CO})_9$ with methanol during the workup.

Discussion

The physical and chemical properties of the $\text{H}_3\text{M}_3(\mu_3\text{-CY})(\text{CO})_9$ series ($\text{M} = \text{Ru}$, $\text{Y} = \text{OCH}_3$, OC_2H_5 , Cl , Br , CO_2CH_3 , C_6H_5 , $\text{C}_6\text{H}_4\text{CH}_3$, H ; $\text{M} = \text{Os}$, $\text{Y} = \text{OCH}_3$, OC_2H_5 , Br) appear, as expected, to be similar in many respects to those of the well-known $\text{Co}_3(\mu_3\text{-CY})(\text{CO})_9$ series. The methylidyne-ruthenium clusters are, however, significantly less stable to oxygen or heat than the osmium or cobalt analogues. Additionally, the ruthenium and osmium clusters can undergo reactions involving loss of dihydrogen not available to the cobalt clusters. While this work has concerned almost exclusively ruthenium clusters, the osmium analogues are expected to behave similarly.

The most significant difference between the methylidyne clusters of ruthenium and of cobalt observed in this work is revealed by the reactions of the halide derivatives with nucleophiles under basic reaction conditions. Both $\text{H}_3\text{Ru}_3(\mu_3\text{-CBr})(\text{CO})_9$ and $\text{Co}_3(\mu_3\text{-CBr})(\text{CO})_9$ form "acylium" cations upon treatment with aluminum trichloride and carboxylic acid derivatives upon subsequent treatment with nucleophiles. However, while the cobalt cluster also forms such products from nucleophiles under basic conditions, e.g., $\text{Co}_3(\mu_3\text{-CCO}_2\text{CH}_3)(\text{CO})_9$ from methanol/triethylamine, $\text{H}_3\text{Ru}_3(\mu_3\text{-CBr})(\text{CO})_9$ gives only ether products. This difference may

be due to the greater propensity of cobalt for carbonylation reactions, but clearly the reasons for it are not understood and stabilities of the respective intermediate cations may be important.

The hydride ligands of $\text{H}_3\text{Ru}_3(\mu_3\text{-COR})(\text{CO})_9$ ($\text{R} = \text{CH}_3$, C_2H_5) enable the cluster to undergo reactions not available to the cobalt analogue. At 100°C under a carbon monoxide atmosphere $\text{H}_3\text{Ru}_3(\mu_3\text{-COCH}_3)(\text{CO})_9$ slowly loses dihydrogen and reverts to $\text{HRu}_3(\mu\text{-COCH}_3)(\text{CO})_{10}$. The $\mu\text{-COCH}_3$ group is favorable because of the stabilization afforded by the $\text{C}^-\text{=OCH}_3^+$ resonance form.⁵ This resonance form is more important for the amino derivatives because of the lower electronegativity of nitrogen and, thus, $\text{H}_3\text{Ru}_3(\mu_3\text{-CNR}_2)(\text{CO})_9$ cannot be formed either by hydrogenation of $\text{HRu}_3(\mu\text{-CNR}_2)(\text{CO})_{10}$ or by attack of NHR_2 on $\text{H}_3\text{Ru}_3(\mu_3\text{-CBr})(\text{CO})_9$.

The methylidyne clusters $\text{H}_3\text{M}_3(\mu_3\text{-CY})(\text{CO})_9$ may be expected to display an even richer chemistry than the cobalt series. These clusters offer possibilities for novel reactions involving loss of dihydrogen and coordination of donor ligands, as well as for coupling reactions involving the methylidyne fragment. Further work in this area is in progress.

Registry No. $\text{H}_3\text{Ru}_3(\mu_3\text{-CBr})(\text{CO})_9$, 73746-95-9; $\text{H}_3\text{Os}_3(\mu_3\text{-CBr})(\text{CO})_9$, 73746-96-0; $\text{H}_3\text{Ru}_3(\mu_3\text{-CCl})(\text{CO})_9$, 73746-97-1; $\text{H}_3\text{Ru}_3(\mu_3\text{-CCO}_2\text{CH}_3)(\text{CO})_9$, 73746-98-2; $\text{H}_3\text{Ru}_3(\mu_3\text{-CC}_6\text{H}_5)(\text{CO})_9$, 73746-99-3; $\text{H}_3\text{Ru}_3(\mu_3\text{-CC}_6\text{H}_4\text{-}o\text{-CH}_3)(\text{CO})_9$, 73747-00-9; $\text{H}_3\text{Ru}_3(\mu_3\text{-CC}_6\text{H}_4\text{-}p\text{-CH}_3)(\text{CO})_9$, 73747-01-0; $\text{H}_3\text{Ru}_3(\mu_3\text{-COC}_2\text{H}_5)(\text{CO})_9$, 73747-02-1; $\text{HRu}_3(\mu\text{-CN}(\text{C}_2\text{H}_5)_2)(\text{CO})_{10}$, 73747-03-2; $\text{H}_3\text{Ru}_3(\mu_3\text{-CH})(\text{CO})_9$, 63280-43-3; $\text{H}_3\text{Ru}_3(\mu_3\text{-COCH}_3)(\text{CO})_9$, 71562-47-5; $\text{H}_3\text{Os}_3(\mu_3\text{-COCH}_3)(\text{CO})_9$, 73747-04-3; BBr_3 , 10294-33-4; BCl_3 , 10294-34-5; methanol, 67-56-1; benzene, 71-43-2; toluene, 108-88-3; ethanol, 64-17-5; diethylamine, 109-89-7.

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Coordination Geometry of the Tridentate Chelating Ligand 2,2'-Bis(*o*-diphenylphosphino)-*trans*-stilbene (bdpps). Crystal Structures of the Complexes (bdpps)CIRh^I·CH₂Cl₂, (bdpps)CIRh^{III}, and (bdpps)Cl₃Ir^{III}

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The crystal and molecular structures of the complexes (bdpps)CIRh^I·CH₂Cl₂, **1**, (bdpps)Cl₃Rh^{III}, **2**, and (bdpps)Cl₃Ir^{III}, **3**, (bdpps = *o*-Ph₂PC₆H₄CH=CHC₆H₄PPh₂-*o*), have been determined by three-dimensional X-ray structural analysis using data collected by counter methods. Compound **1** crystallizes in space group $P\bar{1}$ with $a = 9.3781$ (6) Å, $b = 20.7484$ (10) Å, $c = 9.3768$ (6) Å, $\alpha = 93.12$ (1)°, $\beta = 76.80$ (1)°, $\gamma = 101.26$ (1)°, and $Z = 2$. Crystals of **2** and **3** are isomorphous, of space group $C2/c$, with $Z = 4$ and $a = 17.3288$ (9) Å, $b = 10.6979$ (6) Å, $c = 17.9021$ (9) Å, and $\beta = 99.89$ (1)° for **2** and $a = 17.3352$ (10) Å, $b = 10.7097$ (6) Å, $c = 17.9308$ (9) Å, and $\beta = 99.86$ (1)° for **3**. The structures have been solved by conventional heavy-atom techniques and were refined by least-squares methods to final conventional R factors of 0.036 (**1**, 4428 independent reflections), 0.020 (**2**, 2391 reflections), and 0.033 (**3**, 2698 reflections). Important bond lengths are Rh(I)-Cl = 2.344 (2) Å, Rh(III)-Cl = 2.344 (1) Å, Ir(III)-Cl = 2.359 (1) Å, Rh(I)-P = 2.285 (2) Å, Rh(III)-P = 2.385 (1) Å, Ir(III)-P = 2.383 (1) Å, Rh(I)-C(olefin) = 2.101 (5) Å, Rh(III)-C(olefin) = 2.238 (2) Å, and Ir(III)-C(olefin) = 2.203 (3) Å. In the M(III) derivatives (**2** and **3**), the coordinated olefin is approximately parallel to the P-M-P axis, while in the Rh(I) derivative (**1**), the olefin is approximately perpendicular to this axis. The differences in orientation are shown to arise from a combination of electronic preferences with the simple geometric requirements of the chelating ligand.

Introduction

It has been shown² that diphenyl-*o*-tolylphosphine undergoes a coupling and dehydrogenation reaction on heating with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, in high-boiling alcohols, to give the complex

(bdpps)CIRh^I, **1** (bdpps = *o*-Ph₂PC₆H₄-*t*-CH=CHC₆H₄PPh₂-*o*, **4**), in low yield. Compound **1** is more efficiently prepared by reacting 2,2'-bis(diphenylphosphino)di-benzyl with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$.^{3,4} Subsequent treatment with

(1) To whom correspondence should be addressed.

(2) Bennett, M. A.; Longstaff, P. A. *J. Am. Chem. Soc.* **1969**, *91*, 6266.

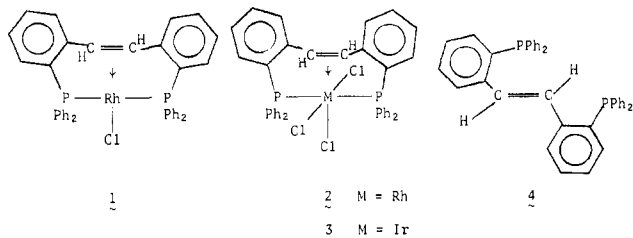
(3) Bennett, M. A.; Clark, P. W.; Robertson, G. B.; Whimp, P. O. *J. Chem. Soc., Chem. Commun.* **1972**, 1011.

Table I. Refinement Details

	(bdpps)ClRh·CH ₂ Cl ₂	(bdpps)Cl ₃ Rh	(bdpps)Cl ₃ Ir
least-squares method	block-diagonal	full-matrix	full-matrix
refinement of extinction parameter ^a	no serious extinction	yes	yes
nonhydrogen atom temperature factors	anisotropic ^b	anisotropic ^b	anisotropic ^b
hydrogen atom contributions	included; ^f hydrogen positions refined	included; hydrogen positions refined	included at positions computed from molecular geometry ^{c,e}
hydrogen atom temperature factors	refined	refined	$B_H = B_C (A^2)$
function minimized	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$
no. of observations (<i>m</i>)	4428	2391	2698
no. of variables (<i>n</i>)	526	261	204
$[\sum w(F_o - F_c)^2 / (m - n)]^{1/2}$	1.30	1.44	1.94
$R = \sum F_o - F_c / \sum F_o $	0.036	0.020	0.033
$Rw = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$	0.043	0.028	0.043
max shift/esd in final cycle	0.09	0.08	0.002
weighting scheme ^g	$w = [\sigma^2(F_o)]^{-1 d}$	$w = [\sigma^2(F_o)]^{-1 d}$	$w = [\sigma^2(F_o)]^{-1 d}$
features in final difference Fourier synthesis	<0.5 e Å ⁻³	<0.4 e Å ⁻³	1.50 Å ⁻³ near the Ir atom and <0.5 e Å ⁻³ elsewhere

^a Reference 9. ^b In the form $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$; deposited with the supplementary material. ^c Assuming the phenyl groupings to be planar with the hydrogen atom in that plane and on the bisector of the C-C-C angle with C-H = 0.95 Å. ^d $\sigma^2(F_o)$ is defined in ref 7. ^e Except for H(17) for which the positional parameters were varied. ^f Except for the hydrogen atoms of the dichloromethane solvate. ^g In each case the weighting scheme analysis shows no serious dependence of $w(|F_o| - |F_c|)^2$ on $|F_o|$ or $(\sin \theta)/\lambda$.

NaCN in refluxing 2-methoxyethanol yields the free ligand 2,2'-bis(*o*-diphenylphosphino)-*trans*-stilbene (bdpps, **4**). The ligand has been shown to form tridentate chelate complexes with planar Rh(I) and Ir(I) and octahedral Ir(III). The Rh(I) and Ir(I) complexes have been shown to oxidatively add either chlorine or HCl to yield octahedral Rh(III) and Ir(III) complexes.⁵ In this paper we report in detail the crystal and molecular structures of the complexes (bdpps)ClRh^I (**1**), (bdpps)Cl₃Rh^{III} (**2**), and (bdpps)Cl₃Ir^{III} (**3**) and consider how



coordination of the tridentate ligand is affected by varying either the metal oxidation state or the transition-metal row. A preliminary account of the X-ray structure of complex **1** has appeared.³

Experimental Section

Collection and Reduction of X-ray Intensity Data. Approximate unit cell dimensions and symmetry information were obtained for crystals of each complex from preliminary Weissenberg and precession photographs. For **1**, the preliminary data were consistent with either of the triclinic space groups *P1* and $\bar{P}1$ and for the isomorphous pair **2** and **3** with either of the monoclinic space groups *Cc* and *C2/c*. Choice of the centrosymmetric alternatives ($\bar{P}1$, *C2/c*) was subsequently confirmed by successful solution and refinement of the structures. Measured crystal densities for **1** are consistent with the inclusion of one molecule of dichloromethane solvent in the lattice per molecule of complex, and *Z* = 2. Crystals of **2** and **3** are solvent free with *Z* = 4 in space group *C2/c*, the metal atom and one chlorine atom are constrained to lie on the crystallographic diad axis and molecules must have exact twofold rotational symmetry. No such constraints are imposed by the packing arrangement in **1**.

Diffraction data were recorded by using a Picker FACS-1 four-circle diffractometer and graphite crystal monochromated copper *K* α radiation ($\lambda = 1.5418$ Å). For each complex, accurate unit cell dimensions and crystal orientation matrices were determined by

least-squares analysis⁶ of the setting angles 2θ , ω , χ , and ϕ for the 12 carefully centered high-angle reflections. The estimated standard deviations in the tabulated cell dimensions were derived directly from the least-squares analysis.

Crystal Data. 1, [*o*-(C₆H₅)₂PC₆H₄-*t*-CH=CHC₆H₄P(C₆H₅)₂-*o*]-ClRh·CH₂Cl₂: *m* = 771.9 daltons, triclinic, space group $\bar{P}1$ [*C*₁^h, No. 2], *a* = 9.3781 (6) Å, *b* = 20.7484 (10) Å, *c* = 9.3768 (6) Å, α = 93.12 (1)°, β = 76.80 (1)°, γ = 101.26 (1)°, *V*_c = 1742.1 Å³, ρ_{obsd} = 1.46 (1) g cm⁻³, ρ_{calcd} = 1.47 g cm⁻³, *Z* = 2, *F*(000) = 784, μ (Cu *K* α) = 72.28 cm⁻¹, *t* = 20 ± 1 °C.

2, [*o*-(C₆H₅)₂PC₆H₄-*t*-CH=CHC₆H₄P(C₆H₅)₂-*o*]-Cl₃Rh: *m* = 757.9 daltons, monoclinic, space group *C2/c* [*C*_{2h}^h, No. 15], *a* = 17.3288 (9) Å, *b* = 10.6979 (6) Å, *c* = 17.9021 (9) Å, β = 99.89 (1)°, *V*_c = 3269.5 Å³, ρ_{obsd} = 1.53 (1) g cm⁻³, ρ_{calcd} = 1.54 g cm⁻³, *Z* = 4, *F*(000) = 1536, μ (Cu *K* α) = 77.06 cm⁻¹, *t* = 20 ± 1 °C.

3, [*o*-(C₆H₅)₂PC₆H₄-*t*-CH=CHC₆H₄P(C₆H₅)₂-*o*]-Cl₃Ir: *m* = 847.2 daltons, monoclinic, space group *C2/c* [*C*_{2h}^h, No. 15], *a* = 17.3352 (10) Å, *b* = 10.7097 (6) Å, *c* = 17.9308 (9) Å, β = 99.86 (1)°, *V*_c = 3279.8 Å³, ρ_{obsd} = 1.73 (1) g cm⁻³, ρ_{calcd} = 1.72 g cm⁻³, *Z* = 4, *F*(000) = 1664, μ (Cu *K* α) = 111.31 cm⁻¹, *t* = 25 ± 1 °C.

Reflection intensity measurement and data reduction procedures were similar to those which we have described previously.⁷ Reflection intensities were recorded in θ - 2θ scan mode ($2\theta_{\text{max}} \approx 125^\circ$). Including standards, 6434, 5127, and 6169 reflections (spanning 1, ca. 1.7, and 2 equivalent sets) were measured for **1**, **2**, and **3**, respectively. Corresponding unique data sets contained 4428, 2391, and 2698 reflections each with $I \geq 3\sigma(I)$. Additional details of the experimental parameters and data collection procedures employed have been tabulated and included in the supplementary material. (For information regarding availability of supplementary material, see the paragraph at the end of this paper.)

During data collection, the intensities of three "standard" reflections were monitored at regular intervals. Data for **3** showed a small (<3% total) time-dependent isotropic intensity loss, apparently due to crystal degradation, and reflection intensities were corrected accordingly. Reflection intensities were reduced to structure factor amplitudes [$|F_o|$] and their estimated standard errors [$\sigma(F_o)$] were assigned as described previously ($p^2 = 0.002$ assumed).⁷ Weak reflections [$I \leq 3\sigma(I)$] and those with uneven backgrounds ($\Delta B > 3\sigma$)⁷ were discarded. Data sets were then sorted and equivalent reflection forms averaged. Statistical *R* values (*R*_s) for the terminal unique data sets are 0.028 (**1**, 4428 reflections), 0.010 (**2**, 2391 reflections), and 0.010 (**3**, 2698 reflections).

Solution and Refinement of the Structures. The structures were solved by conventional Patterson and Fourier syntheses and were refined by least-squares methods (block-diagonal for **1**; full matrix

(4) Bennett, M. A.; Clark, P. W. *J. Organomet. Chem.* **1976**, *110*, 367.
(5) Bennett, M. A.; Johnson, R. N.; Tomkins, I. B. *J. Organomet. Chem.* **1976**, *118*, 205.

(6) The Busing and Levy programs (*Acta Crystallogr.* **1967**, *22*, 457) for four-circle diffractometers were used for all phases of diffractometer control.

(7) Robertson, G. B.; Whimp, P. O. *J. Am. Chem. Soc.* **1975**, *97*, 1051.

Table II. Final Atomic Coordinates for (bdpps)ClRh^I·CH₂Cl₂^a

ATOM	X/A	Y/B	Z/C
RH	0.20279(1)	0.26897(1)	0.27108(1)
CL	-0.00984(12)	0.30430(15)	0.42163(12)
CL(15)	0.47914(26)	0.21790(12)	0.66431(23)
CL(25)	0.69761(23)	0.26793(13)	0.82734(24)
P(1)	0.30669(12)	0.36303(15)	0.17376(11)
P(2)	0.10413(12)	0.16139(15)	0.37357(11)
C(15)	0.6471(19)	0.2626(12)	0.6853(17)
C(117)	0.4255(15)	0.2827(12)	0.2865(14)
C(117)	0.3572(14)	0.2208(12)	0.1427(14)
C(101)	0.2628(15)	0.4401(12)	0.2522(14)
C(102)	0.3029(17)	0.4620(13)	0.3033(15)
C(103)	0.3580(18)	0.5160(13)	0.4530(16)
C(104)	0.1756(17)	0.5513(13)	0.3740(17)
C(105)	0.1367(17)	0.5318(13)	0.2677(17)
C(106)	0.1707(16)	0.4757(12)	0.1949(15)
C(111)	0.6040(15)	0.3698(12)	0.1714(14)
C(112)	0.8376(15)	0.3140(12)	0.2273(14)
C(113)	0.6810(15)	0.3177(12)	0.2402(15)
C(114)	0.7078(15)	0.3747(12)	0.2126(15)
C(115)	0.7562(15)	0.4278(12)	0.1548(15)
C(116)	0.6138(15)	0.4258(12)	0.1346(15)
C(121)	0.2849(15)	0.3639(12)	-0.0121(14)
C(122)	0.1433(15)	0.3386(12)	-0.0363(15)
C(123)	0.1615(17)	0.3396(13)	-0.1784(16)
C(124)	0.2240(18)	0.3638(13)	-0.2893(16)
C(125)	0.3635(17)	0.3884(13)	-0.2674(15)
C(126)	0.3951(16)	0.3891(12)	-0.1295(15)
C(201)	0.1126(15)	0.1385(12)	0.8555(14)
C(202)	0.0495(17)	0.1749(12)	0.6719(15)
C(203)	0.0472(18)	0.1594(12)	0.8124(15)
C(204)	0.0660(16)	0.1079(12)	0.6425(15)
C(205)	0.1736(16)	0.0716(12)	0.7283(15)
C(206)	0.1762(16)	0.0871(12)	0.8846(15)
C(211)	0.2093(15)	0.1113(12)	0.2916(14)
C(212)	0.3210(15)	0.1476(12)	0.1349(14)
C(213)	0.3985(15)	0.1137(12)	0.0189(15)
C(214)	0.3642(16)	0.0458(12)	0.0098(15)
C(215)	0.2551(16)	0.0106(12)	0.1160(16)
C(216)	0.1766(15)	0.0430(12)	0.2311(15)
C(221)	-0.0003(15)	0.1319(12)	0.3626(14)
C(222)	-0.1290(16)	0.1467(12)	0.2385(15)
C(223)	-0.2749(17)	0.1272(12)	0.2229(16)
C(224)	-0.3799(16)	0.0624(12)	0.3295(17)
C(225)	-0.3417(17)	0.0774(12)	0.4588(17)
C(226)	-0.1948(16)	0.0971(12)	0.4716(16)

ATOM	X/A	Y/B	Z/C	B(A ²)
H(102)	0.360(5)	0.436(2)	0.417(5)	5.2(11)
H(103)	0.292(7)	0.523(3)	0.843(6)	8.0(16)
H(104)	0.153(7)	0.590(3)	0.492(6)	8.9(17)
H(105)	0.771(6)	0.848(2)	0.239(5)	7.0(14)
H(106)	0.159(5)	0.462(2)	0.099(4)	5.2(11)
H(113)	0.707(5)	0.279(2)	0.276(5)	5.9(13)
H(114)	0.695(5)	0.375(2)	0.222(4)	4.1(10)
H(115)	0.834(5)	0.467(2)	0.135(4)	4.0(10)
H(116)	0.692(5)	0.463(2)	0.103(4)	4.7(11)
H(122)	0.765(6)	0.325(2)	0.039(5)	6.6(13)
H(123)	0.714(6)	0.323(2)	-0.174(5)	6.0(12)
H(124)	0.210(5)	0.358(2)	-0.307(4)	5.0(11)
H(125)	0.450(5)	0.440(2)	-0.342(7)	11.1(20)
H(126)	0.514(6)	0.448(2)	-0.131(5)	6.0(13)
H(202)	-0.021(5)	0.209(2)	0.684(4)	5.1(11)
H(203)	-0.026(6)	0.193(3)	0.886(5)	7.3(14)
H(204)	0.110(5)	0.095(2)	0.943(4)	4.3(10)
H(205)	0.212(7)	0.032(3)	0.765(6)	9.8(18)
H(206)	0.216(6)	0.088(2)	0.808(5)	6.3(13)
H(213)	0.475(5)	0.140(2)	-0.096(4)	5.2(11)
H(214)	0.413(5)	0.021(2)	-0.074(5)	5.7(12)
H(215)	0.238(5)	-0.032(2)	0.102(4)	5.0(11)
H(216)	0.197(5)	0.017(2)	0.304(4)	5.7(12)
H(222)	-0.262(5)	0.186(2)	0.172(4)	5.2(11)
H(223)	-0.358(6)	0.133(3)	0.147(5)	7.5(15)
H(224)	-0.485(6)	0.078(3)	0.322(6)	8.2(15)
H(225)	-0.414(7)	0.060(3)	0.542(6)	9.5(16)
H(226)	-0.164(5)	0.069(2)	0.551(5)	5.5(12)
H(117)	0.438(5)	0.226(2)	0.331(4)	3.7(9)
H(217)	0.388(5)	0.238(2)	0.039(5)	5.6(12)

^a Estimated standard deviations in the least significant figures are given in parentheses. Anisotropic thermal parameters are contained in the supplementary material of this paper.

for 2 and 3). In the course of refinement, data for all three complexes were corrected for specimen absorption effects.⁸ For 2 and 3 data

Table III. Final Atomic Coordinates for (bdpps)Cl₃Rh^{III}

ATOM	X/A	Y/B	Z/C
RH	0.0	0.23800(12)	0.25
CL(1)	0.0	0.01864(16)	0.25
CL(2)	-0.06167(13)	0.24269(14)	0.35460(13)
P	0.11863(13)	0.23126(14)	0.34000(13)
C(11)	0.11125(12)	0.37324(19)	0.39340(11)
C(12)	0.06431(11)	0.46173(18)	0.35091(11)
C(13)	0.04396(13)	0.57075(20)	0.38462(13)
C(14)	0.07095(15)	0.58992(25)	0.46113(15)
C(15)	0.11876(16)	0.50552(27)	0.50251(15)
C(16)	0.13948(14)	0.39571(25)	0.46989(13)
C(17)	0.03016(12)	0.43724(17)	0.26787(11)
C(21)	0.21042(13)	0.23934(16)	0.30422(12)
C(22)	0.22245(13)	0.15966(20)	0.24548(13)
C(23)	0.29222(14)	0.16408(25)	0.21809(14)
C(24)	0.34971(18)	0.24721(22)	0.24821(19)
C(25)	0.33855(15)	0.32519(27)	0.30604(17)
C(26)	0.26921(13)	0.32192(22)	0.33389(14)
C(31)	0.13203(12)	0.10073(20)	0.40624(11)
C(32)	0.17890(14)	0.00099(21)	0.39428(14)
C(33)	0.18629(16)	-0.09870(24)	0.44400(16)
C(34)	0.15252(14)	-0.10005(23)	0.50594(14)
C(35)	0.10430(15)	-0.00291(24)	0.51785(13)
C(36)	0.09357(14)	0.09718(23)	0.46838(12)

ATOM	X/A	Y/B	Z/C	B(A ²)
H(13)	0.008(1)	0.629(2)	0.354(1)	3.7(5)
H(14)	0.054(1)	0.664(2)	0.484(1)	5.4(6)
H(15)	0.136(1)	0.515(2)	0.554(1)	5.2(6)
H(16)	0.172(1)	0.340(2)	0.497(1)	2.6(5)
H(22)	0.181(1)	0.101(2)	0.223(1)	3.5(5)
H(23)	0.295(1)	0.118(2)	0.175(1)	4.5(6)
H(24)	0.400(2)	0.257(2)	0.224(2)	6.8(9)
H(25)	0.375(2)	0.378(2)	0.326(1)	6.3(7)
H(26)	0.264(1)	0.375(2)	0.372(1)	3.6(5)
H(32)	0.202(1)	0.003(2)	0.354(1)	4.3(6)
H(33)	0.218(1)	-0.161(2)	0.433(1)	4.0(6)
H(34)	0.158(1)	-0.176(2)	0.545(1)	5.2(5)
H(35)	0.075(1)	-0.004(2)	0.563(1)	5.1(6)
H(24)	0.044(1)	0.168(2)	0.474(1)	3.7(5)
H(17)	0.081(1)	0.445(2)	0.236(1)	3.2(4)

were also corrected for extinction according to the method of Zachariasen.⁹ Data for 1 exhibited no serious extinction and no correction was applied. For 2 and 3, atomic scattering factors, together with anomalous dispersion corrections, were taken from ref 10. For 1, nonhydrogen atom scattering factors were taken from ref 11, hydrogen atom scattering factors were taken from ref 12, and anomalous dispersion corrections were taken from ref 13. Refinement details are summarized in Table I. Final atom coordinates, together with standard error estimates derived by matrix inversion, are listed in Tables II (1), III (2), and IV (3). Tables of atom thermal parameters and of terminal $10|F_o|$ and $10|F_c|$ values (electrons) have been included in the supplementary material. Computational details are given in ref 14.

- (8) Corrections for 1 were calculated by numerical integration using a grid of $14 \times 4 \times 8$ parallel to a , b^* , and c^* , and corrections for 2 and 3 were calculated by an analytical procedure (De Meulenaer, J.; Tompa, H. *Acta Crystallogr.* 1965, 19, 1014).
- (9) Zachariasen, W. H. *Acta Crystallogr.* 1967, 23, 558; *Acta Crystallogr., Sect. A* 1968, 24, 212.
- (10) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.
- (11) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. III, p 202.
- (12) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* 1965, 42, 3175.
- (13) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* 1970, 53, 1891.
- (14) Computer programs were those in the ANUCRYS package collected and assembled by Drs. P. O. Whimp and D. Taylor. Individual programs are described by: Ferguson, J.; Mau, A. W.-H.; Whimp, P. O. *J. Am. Chem. Soc.* 1979, 101, 2363. Calculations were performed on the UNIVAC 1108 (later 1100/42) computer of the Australian National University Computer Services Centre. Molecular diagrams were produced by using ORTEP.

Table IV. Final Atomic Coordinates for (bdpps)Cl₃Ir^{III}

ATOM	X/A	Y/B	Z/C	B(Å ²)
IR	0.0	0.23899(1)	0.25	
CL(1)	0.0	0.01869(10)	0.25	
CL(2)	-0.06239(6)	0.24316(6)	0.57700(5)	
P	-0.11820(6)	0.23136(7)	0.15996(5)	
C(11)	0.1109(2)	0.3731(3)	0.7937(2)	
C(12)	0.0646(2)	0.4679(3)	0.7508(2)	
C(13)	0.0442(2)	0.5711(3)	0.3878(2)	
C(14)	0.0708(2)	0.5905(4)	0.4601(2)	
C(15)	0.1185(3)	0.5058(5)	0.5023(2)	
C(16)	0.1402(2)	0.3956(4)	0.4699(2)	
C(17)	0.0390(2)	0.4343(3)	0.2675(2)	
C(21)	0.2006(2)	0.2395(3)	0.3039(2)	
C(22)	0.2223(2)	0.1597(4)	0.2456(2)	
C(23)	0.2920(2)	0.1633(4)	0.2185(2)	
C(24)	0.3498(3)	0.2466(3)	0.2481(4)	
C(25)	0.3386(2)	0.3257(4)	0.3062(2)	
C(26)	0.2690(2)	0.3219(3)	0.3340(2)	
C(31)	0.1320(2)	0.1014(3)	0.4060(2)	
C(32)	0.1789(2)	0.0014(3)	0.7938(2)	
C(33)	0.1883(2)	-0.0988(4)	0.4434(2)	
C(34)	0.1515(2)	-0.0996(4)	0.5056(2)	
C(35)	0.1074(3)	-0.0019(4)	0.5175(2)	
C(36)	0.0932(2)	0.0975(4)	0.4681(2)	
ATOM	X/A	Y/B	Z/C	B(Å ²)
H(13)	0.011	0.633	0.753	3.7
H(14)	0.054	0.665	0.484	4.5
H(15)	0.138	0.523	0.555	4.7
H(16)	0.174	0.334	0.500	4.1
H(22)	0.181	0.100	0.224	3.6
H(23)	0.301	0.108	0.178	4.3
H(24)	0.398	0.250	0.229	4.9
H(25)	0.380	0.384	0.328	4.7
H(26)	0.261	0.379	0.375	3.7
H(32)	0.205	0.001	0.350	4.0
H(33)	0.223	-0.170	0.434	4.8
H(34)	0.160	-0.169	0.541	4.4
H(35)	0.078	-0.004	0.561	4.2
H(36)	0.058	0.166	0.477	3.9
H(17)	0.080(2)	0.443(3)	0.235(2)	2.6

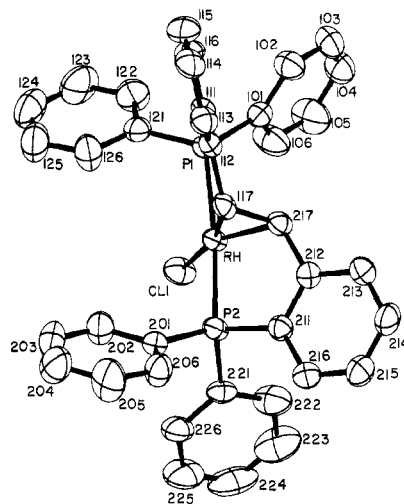


Figure 1. Molecular geometry and atom numbering in (bdpps)ClRh^I. In Figures 1–4, ellipsoids are scaled to include 50% probability. Carbon atoms are labeled with a number alone, and hydrogen atoms are omitted for clarity.

stantial variations, even between closely related complexes. Thus metal–ligand distances in **1** are shorter (by 0.02–0.05 Å) than the corresponding distances in the very similar complex $[t\text{-Bu}_2\text{P}(\text{CH}_2)_2\text{-}t\text{-CH}=\text{CH}(\text{CH}_2)_2\text{P-}t\text{-Bu}_2]\text{ClRh}^{\text{I}}$.¹⁶ In this case, the differences probably reflect increased crowding around the metal atom due to the bulky *tert*-butyl substituents of the phosphine ligand. The M–P and M–C(olefin) distances in **1** are similar to those in the complex $[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{-}t\text{-CH}=\text{CH}(\text{CH}_2)_2\text{PPh}_2]\text{ClIr}^{\text{I}}$,¹⁷ but the M–Cl distance differs substantially (ca. 0.05 Å shorter in **1**). The Rh–P distances in **1** [2.283 (2) and 2.287 (2) Å] lie at the extreme low limit of values reported for the phosphorus trans to phosphorus, both with chelating^{18,19} and nonchelating²⁰ phosphines. The Rh–(I)–Cl distance in **1** [2.344 (2) Å] is toward the low limit of reported Rh–Cl values trans to a trans directing ligand.²¹ In

Results

Description of the Structures. Crystals of all three complexes (**1**, **2**, and **3**) contain discrete monomeric molecular units separated by normal van der Waals contacts. Crystals of **1** contain one molecule of solvent (dichloromethane) per molecule of complex. Molecules of **1** are essentially square planar, with the phosphorus atoms of the tridentate bdpps ligand (**4**) occupying mutually trans sites, and have very approximate twofold rotational symmetry about the Rh–Cl(1) bond direction. The molecular stereochemistry is shown in Figure 1, which also serves to define the atom-numbering scheme, and the crystal packing arrangement is illustrated by the stereopair of Figure 2.¹⁵ Bond distances and bond angles are listed in Table V.

Crystals of **2** and **3** are isomorphous and solvent free. Molecules are trans octahedral and are constrained by crystal-packing requirements to have exact twofold rotational symmetry about the M–Cl(1) bond direction. For comparison, molecules of **2** and **3** are shown together in Figure 3 along with the atom-numbering scheme. The packing arrangement is illustrated in Figure 4, and bond lengths and bond angles for the two complexes are compared in Table VI.

Discussion

(*o*-Ph₂PC₆H₄-*t*-CH=CHC₆H₄PPh₂-*o*)ClRh^I, **1**. Metal–ligand distances in Rh(I)–phosphine complexes show sub-

- (16) Mason, R.; Scollary, G.; Moyle, B.; Hardcastle, K. I.; Shaw, B. L.; Moulton, C. J. *J. Organomet. Chem.* **1976**, *113*, C49.
- (17) Clark, G. R.; Mazid, M. A.; Russell, D. R.; Clark, P. W. *J. Organomet. Chem.* **1979**, *166*, 109.
- (18) For example: 2.288 Å in $[\text{PhP}[(\text{CH}_2)_2\text{PPh}_2]_2]\text{ClRh}$ (Nappier, T. E.; Meek, D. W.; Kirchner, R. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 4194), 2.291 Å in $[\{\text{Ph}_2\text{PC}(\text{CF}_3)_2\text{CPPh}_2\text{Rh}\}]^+$ (Einstein, F. W. B.; Hampton, C. R. S. M. *Can. J. Chem.* **1971**, *49*, 1901), 2.300 Å in $[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{PPh}_2](\text{CO})\text{Rh}$ (Alcock, N. W.; Brown, J. M.; Jeffery, J. C. *J. Chem. Soc., Dalton Trans.* **1976**, 583), 2.306 Å in $[\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\text{Rh}\}]^+$ (Hall, H. C.; Kilbourn, B. T.; Taylor, K. A. *J. Chem. Soc. A* **1970**, 2539), 2.316 Å in $[t\text{-Bu}_2\text{P}(\text{CH}_2)_2\text{-}t\text{-CH}=\text{CH}(\text{CH}_2)_2\text{P-}t\text{-Bu}_2]\text{ClRh}$,¹⁶ 2.336 Å in $[\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{PPh}_2\}(\text{C}_2\text{H}_5\text{OH})(\text{CO})\text{Rh}\}]^+$ (Alcock, N. W.; Brown, J. M.; Jeffery, J. C. *J. Chem. Soc., Dalton Trans.* **1977**, 888), 2.338 Å in $[\{\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2\text{O})_3(\text{CH}_2)_2\text{PPh}_2\}(\text{CO})(\text{H}_2\text{O})\text{Rh}\}]^+$ (Alcock, N. W.; Brown, J. M.; Jeffery, J. C. *J. Chem. Soc., Dalton Trans.* **1976**, 583), and 2.365 Å in $[t\text{-Bu}_2\text{P}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{P}(\text{CO})\text{ClRh}]_2$ (March, F. C.; Mason, R.; Thomas, K. M.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1975**, 584).
- (19) A cursory glance at the variations in Rh–P bond length in complexes with bidentate phosphines spanning trans positions suggests that at the extremes, the smaller the P–Rh–P angle the shorter the Rh–P distance. However, the correlation, which would be consistent with the operation of a “constant overlap criterion”, is not good.
- (20) For example: 2.291 Å in $(\text{PPh}_3)_2[\text{NC}(\text{CF}_3)_2][\text{C}(\text{NMe})(\text{CH}_2)_2\text{NMe}]\text{Rh}$ (Doyle, M. J.; Lappert, M. F.; McLaughlin, G. M.; McMeeking, J. *J. Chem. Soc., Dalton Trans.* **1974**, 1494), from 2.304 to 2.338 Å in the orange and red allotropes of $(\text{PPh}_3)_3\text{ClRh}$ (Bennett, M. J.; Donaldson, P. B. *Inorg. Chem.* **1977**, *16*, 655), 2.329 Å in $[\text{Rh}(\text{CO})(\text{PPh}_3)_2][\text{C}(\text{CN})_6][(\text{PPh}_3)_2(\text{CO})\text{Rh}]$ (Schlödter, R.; Ibers, J. A. *Ibid.* **1974**, *13*, 2870), 2.336 Å in $(\text{PPh}_3)_2(\text{CS})\text{ClRh}$ (De Boer, J. L.; Rogers, D.; Skapski, A. C.; Troughton, P. G. H.; *J. Chem. Soc., Chem. Commun.* **1966**, 756), and 2.352 Å to PPh₃ in $(\text{PPh}_3)(\text{PF}_2\text{NEt}_2)_2\text{ClRh}$ (but note 2.215 Å to PF₂NEt₂) (Bennett, M. A.; Robertson, G. B.; Whimp, P. O.; Turney, T. W. *Ibid.*, **1971**, 762).

(15) Figures 1–4 were all drawn by using ORTEP. Hydrogen atoms have been omitted for clarity and thermal ellipsoids have been scaled to include 50% probability.

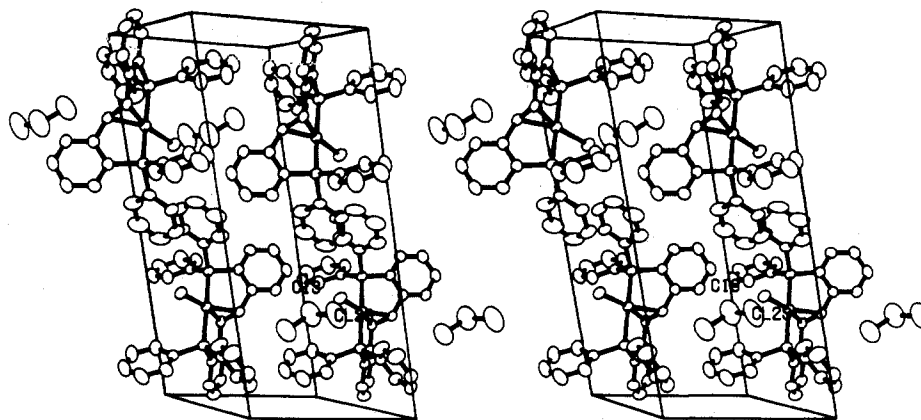


Figure 2. A stereoscopic pair illustrating the unit cell contents for (bdpps)ClRh^I·CH₂Cl₂ viewed approximately along *a*.

Table V. Bond Lengths and Interbond Angles for (bdpps)ClRh^I·CH₂Cl₂ (1)

		(A) Principal Bond Lengths (Å)				
Rh-Cl	2.344 (2)	Rh-P(1)	2.287 (2)	Rh-P(2)	2.283 (2)	
Rh-C(117)	2.107 (5)	Rh-C(217)	2.096 (4)	P(1)-C(101)	1.811 (4)	
P(1)-C(111)	1.805 (5)	P(1)-C(121)	1.809 (4)	P(2)-C(201)	1.813 (5)	
P(2)-C(211)	1.803 (4)	P(2)-C(221)	1.831 (5)			
C(112)-C(117)	1.486 (5)	C(212)-C(217)	1.491 (6)	C(117)-C(217)	1.436 (6)	
C(117)-H(117)	0.96 (4)	C(217)-H(217)	1.01 (4)			
Cl(1S)-C(1S)	1.698 (8)	Cl(2S)-C(1S)	1.775 (8)			
		(B) Principal Interbond Angles (Deg)				
Cl-Rh-P(1)	94.30 (6)	Cl-Rh-P(2)	91.92 (6)	Cl-Rh-C(117)	154.3 (1)	
Cl-Rh-C(217)	165.7 (1)	P(1)-Rh-P(2)	170.79 (4)	P(1)-Rh-C(117)	83.5 (1)	
P(1)-Rh-C(217)	88.5 (1)	P(2)-Rh-C(117)	93.8 (1)	P(2)-Rh-C(217)	83.8 (1)	
C(117)-Rh-C(217)	39.9 (2)					
Rh-P(1)-C(101)	120.9 (2)	Rh-P(1)-C(111)	102.9 (1)	Rh-P(1)-C(121)	114.0 (1)	
Rh-P(2)-C(201)	120.5 (1)	Rh-P(2)-C(211)	103.7 (1)	Rh-P(2)-C(221)	114.6 (1)	
C(101)-P(1)-C(111)	104.8 (2)	C(101)-P(1)-C(121)	104.1 (2)	C(111)-P(1)-C(121)	109.3 (2)	
C(201)-P(2)-C(211)	108.4 (2)	C(201)-P(2)-C(221)	104.2 (2)	C(211)-P(2)-C(221)	104.2 (2)	
C(211)-C(212)-C(217)	121.3 (3)	C(212)-C(217)-C(117)	120.1 (4)			
C(111)-C(112)-C(117)	121.0 (4)	C(112)-C(117)-C(217)	120.7 (3)			
		(C) Phenyl Ring				
atoms	<i>m</i> = 1, <i>n</i> = 0	<i>m</i> = 1, <i>n</i> = 1	<i>m</i> = 1, <i>n</i> = 2	<i>m</i> = 2, <i>n</i> = 0	<i>m</i> = 2, <i>n</i> = 1	<i>m</i> = 2, <i>n</i> = 2
Bond Lengths (Å) ^a						
P(<i>m</i>)-C(<i>mn</i> 1)	1.811 (4)	1.805 (5)	1.809 (4)	1.813 (5)	1.803 (4)	1.831 (5)
C(<i>mn</i> 1)-C(<i>mn</i> 2)	1.394 (7)	1.399 (6)	1.395 (7)	1.379 (7)	1.400 (5)	1.372 (8)
C(<i>mn</i> 2)-C(<i>mn</i> 3)	1.370 (8)	1.392 (7)	1.384 (8)	1.377 (8)	1.400 (5)	1.388 (8)
C(<i>mn</i> 3)-C(<i>mn</i> 4)	1.366 (10)	1.393 (6)	1.335 (7)	1.365 (9)	1.387 (6)	1.358 (8)
C(<i>mn</i> 4)-C(<i>mn</i> 5)	1.354 (10)	1.367 (8)	1.367 (10)	1.377 (7)	1.376 (6)	1.377 (10)
C(<i>mn</i> 5)-C(<i>mn</i> 6)	1.394 (8)	1.382 (8)	1.390 (8)	1.395 (7)	1.383 (6)	1.397 (8)
C(<i>mn</i> 6)-C(<i>mn</i> 1)	1.386 (8)	1.394 (6)	1.372 (6)	1.388 (7)	1.393 (7)	1.377 (6)
Interbond Angles (Deg)						
P(<i>m</i>)-C(<i>mn</i> 1)-C(<i>mn</i> 2)	118.6 (4)	113.7 (3)	117.2 (3)	117.3 (4)	113.7 (3)	117.2 (3)
P(<i>m</i>)-C(<i>mn</i> 1)-C(<i>mn</i> 6)	123.1 (3)	125.7 (4)	124.7 (4)	124.3 (2)	125.7 (3)	124.0 (4)
C(<i>mn</i> 2)-C(<i>mn</i> 1)-C(<i>mn</i> 6)	118.1 (4)	120.2 (4)	118.1 (4)	118.4 (4)	120.2 (4)	118.8 (5)
C(<i>mn</i> 1)-C(<i>mn</i> 2)-C(<i>mn</i> 3)	120.7 (6)	118.8 (4)	120.2 (4)	120.4 (6)	118.5 (4)	120.7 (4)
C(<i>mn</i> 2)-C(<i>mn</i> 3)-C(<i>mn</i> 4)	120.5 (6)	119.8 (5)	121.5 (6)	121.3 (5)	120.5 (4)	120.6 (6)
C(<i>mn</i> 3)-C(<i>mn</i> 4)-C(<i>mn</i> 5)	120.2 (5)	121.4 (5)	119.0 (6)	119.5 (5)	120.4 (4)	119.6 (6)
C(<i>mn</i> 4)-C(<i>mn</i> 5)-C(<i>mn</i> 6)	120.3 (6)	119.3 (4)	121.4 (5)	119.5 (6)	120.1 (4)	119.9 (5)
C(<i>mn</i> 5)-C(<i>mn</i> 6)-C(<i>mn</i> 1)	120.2 (5)	120.5 (5)	119.8 (5)	120.8 (4)	120.2 (4)	120.4 (5)

^a The C-H bond lengths ranged from 0.83 (6) to 1.10 (5) Å and averaged 0.95 (6) Å.

contrast, the corresponding distance in [*t*-Bu₂P(CH₂)₂-*t*-CH=CH(CH₂)₂P-*t*-Bu₂]ClRh [2.398 (4) Å] is at the upper limit for Rh(I)-Cl.

The Rh-C(olefin) distances in 1 [2.096 (4) and 2.107 (5) Å] are equal within experimental error and compare well with

equivalent values [2.10–2.12 Å] in a number of bis(olefin) complexes of Rh(I).²² The C=C(olefin) distance [1.436 (6) Å] is significantly longer than those observed in (acac)(C₂H₄)₂Rh^I [1.390 (7) Å] and (acac)(nor-

(21) For example: 2.376 and 2.404 Å in the red and orange allotropes of (PPh₃)₂ClRh (Bennett, M. J.; Donaldson, P. B. *Inorg. Chem.* 1977, 16, 655), 2.375 Å *trans* to (PF₂NEt₂) in (PPh₂)(PF₂NEt₂)₂ClRh (Bennett, M. A.; Robertson, G. B.; Whimp, P. O.; Turney, T. W. *J. Chem. Soc., Chem. Commun.* 1971, 762), 2.375 Å in *trans*-(PPh₃)₂(C₂F₄)ClRh (Hitchcock, P. B.; McPartlin, M.; Mason, R. *Ibid.* 1969, 1367), and 2.381 Å in [PhP[(CH₂)₃PPh₂]₂]ClRh (Nappier, T. E.; Meek, D. W.; Kirchner, R. M.; Ibers, J. A. *J. Am. Chem. Soc.* 1973, 95, 4194).

(22) The mean Rh-C(olefin) and C=C(olefin) distances, respectively, are 2.117 and 1.390 Å in (acac)(C₂H₄)₂Rh (Russell, D. R.; Evans, J. A. *J. Chem. Soc., Chem. Commun.* 1971, 197. Evans, J. A.; Russell, D. R.; Tucker, P. A., unpublished results), 2.103 and 1.409 Å in (acac)(1,5-cyclooctadiene)Rh (Tucker, P. A.; Scutcher, W.; Russell, D. R. *Acta Crystallogr., Sect. B* 1975, 31, 592), 2.099 and 1.379 Å in (acac)(norbornadiene)Rh (Russell, D. R., private communication), and 2.12 and 1.44 Å in [(1,5-cyclooctadiene)ClRh]₂ (Ibers, J. A.; Synder, R. G. *Acta Crystallogr.* 1962, 15, 923).

Table VI. Bond Lengths and Interbond Angles for the Complexes (bdpps)Cl₃Rh^{III} (2) and (bdpps)Cl₃Ir^{III} (3)

atoms	M = Rh	M = Ir	atoms	M = Rh	M = Ir	
Principal Bond Lengths (Å)						
M-Cl(1)	2.346 (1)	2.359 (1)	M-Cl(2)	2.342 (1)	2.358 (1)	
M-P	2.385 (1)	2.383 (1)	M-C(17)	2.238 (2)	2.203 (3)	
P-C(11)	1.811 (2)	1.816 (3)	P-C(21)	1.821 (2)	1.818 (3)	
P-C(31)	1.816 (2)	1.818 (4)	C(12)-C(17)	1.501 (3)	1.513 (4)	
C(17)-C(17 ^b)	1.367 (4)	1.386 (5)	C(17)-H(17)	1.02 (2)	0.97 (3)	
Principal Interbond Angles (Deg)						
P-M-Cl(1)	88.27 (1)	88.05 (2)	P-M-Cl(2)	84.90 (2)	84.86 (4)	
P-M-Cl(2 ^b)	95.17 (2)	95.21 (4)	P-M-P ^b	176.54 (2)	176.09 (4)	
P-M-C(17)	74.52 (5)	74.30 (9)	P-M-C(17 ^b)	108.93 (5)	109.59 (9)	
Cl(1)-M-Cl(2)	91.23 (1)	91.07 (2)	Cl(1)-M-C(17)	162.23 (5)	161.66 (9)	
Cl(2)-M-Cl(2 ^b)	177.54 (2)	177.84 (3)	Cl(2)-M-C(17)	91.61 (6)	92.21 (8)	
C(17)-M-C(17 ^b)	35.5 (1)	36.7 (2)	M-P-C(11)	101.57 (7)	101.5 (1)	
M-P-C(21)	117.76 (7)	117.9 (1)	M-P-C(31)	117.50 (7)	117.4 (1)	
C(11)-P-C(21)	106.97 (9)	108.0 (2)	C(11)-P-C(31)	108.19 (11)	107.1 (2)	
C(21)-P-C(31)	104.16 (9)	104.9 (2)	C(11)-C(12)-C(17)	118.2 (2)	118.0 (3)	
C(13)-C(12)-C(17)	121.5 (2)	121.5 (3)	C(12)-C(17)-C(17 ^b)	124.5 (2)	123.2 (4)	
C(12)-C(17)-H(17)	115 (1)	99 (2)				
Phenyl Ring Bond Lengths (Å)						
P-C(n1)	1.811 (2)	1.816 (3)	1.821 (2)	1.818 (3)	1.816 (2)	1.818 (4)
C(n1)-C(n2)	1.387 (3)	1.377 (5)	1.397 (3)	1.383 (5)	1.380 (3)	1.390 (5)
C(n2)-C(n3)	1.386 (3)	1.393 (4)	1.381 (3)	1.387 (6)	1.381 (3)	1.386 (7)
C(n3)-C(n4)	1.384 (3)	1.389 (5)	1.375 (4)	1.375 (5)	1.360 (3)	1.387 (6)
C(n4)-C(n5)	1.356 (4)	1.363 (7)	1.369 (4)	1.378 (6)	1.373 (3)	1.377 (6)
C(n5)-C(n6)	1.388 (3)	1.395 (6)	1.378 (3)	1.379 (5)	1.382 (3)	1.379 (5)
C(n6)-C(n1)	1.394 (3)	1.393 (5)	1.384 (3)	1.395 (5)	1.392 (3)	1.395 (5)
Phenyl Ring Interbond Angles (Deg)						
P-C(n1)-C(n2)	111.8 (1)	111.1 (2)	119.3 (2)	120.2 (3)	120.3 (2)	121.5 (3)
P-C(n1)-C(n6)	128.2 (2)	128.0 (3)	121.8 (2)	120.9 (3)	121.1 (2)	119.5 (3)
C(n2)-C(n1)-C(n6)	119.7 (2)	120.6 (3)	118.9 (2)	118.8 (4)	118.6 (2)	118.9 (4)
C(n1)-C(n2)-C(n3)	120.3 (2)	120.5 (3)	120.0 (2)	120.2 (4)	120.3 (3)	120.6 (3)
C(n2)-C(n3)-C(n4)	119.2 (2)	118.5 (4)	120.2 (2)	120.4 (4)	120.9 (3)	119.8 (4)
C(n3)-C(n4)-C(n5)	120.8 (2)	121.0 (4)	120.3 (2)	119.8 (4)	119.6 (2)	120.1 (4)
C(n4)-C(n5)-C(n6)	120.9 (2)	120.9 (4)	120.2 (2)	120.2 (4)	120.4 (2)	120.5 (4)
C(n5)-C(n6)-C(n1)	119.0 (2)	118.2 (4)	120.5 (2)	120.5 (4)	120.2 (2)	120.1 (4)

^a For the Rh(III) complex, all hydrogen atoms were refined. The C-H distances range from 0.87 (3) to 1.06 (3) Å and average 0.95 (4) Å.

^b Refers to atoms related to those in Tables III and IV by the operation $-x, y, 1/2 - z$.

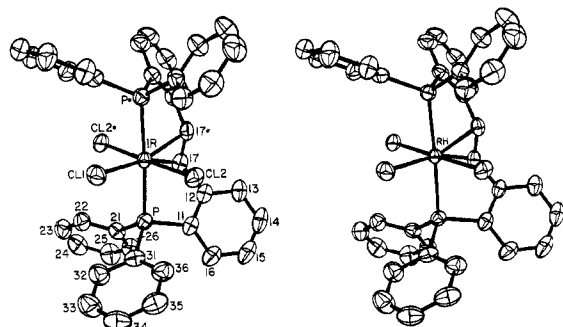


Figure 3. A comparison of the molecular geometries of (bdpps)Cl₃Rh and (bdpps)Cl₃Ir. The atom numbering shown in the Ir complex also applies to the Rh complex. Carbon atoms are labeled with a number alone, those starred are related to atoms in Tables VI and IV by the operation $-x, y, 1/2 - z$. Hydrogen atoms are omitted for clarity.

bornadiene)Rh^I [1.373 (15) Å] (acac = acetylacetonate²²). As expected, the longer C=C(olefin) distance in **1** is associated with increased tetrahedral character at the olefinic carbons. The increased tetrahedral character, which loosely speaking is a further measure of the total metal-ligand bonding interaction, is reflected in increased bend-back²³ at the olefinic

carbons. In **1** the dihedral angle between the C(217)-C(212)-H(217) and C(117)-C(112)-H(117) planes (Table VII) is 55° compared with ca. 35° in (acac)(C₂H₄)₂Rh^I.²² Both the dihedral angles (ca. 28 and 33°, respectively) and the C=C(olefin) distances [1.367 (4) and 1.386 (5) Å] in the analogous Rh(III), **2**, and Ir(III), **3**, complexes are significantly smaller than those in **1**.

(*o*-Ph)₂PC₆H₄-*t*-CH=CHC₆H₄PPh₂-*o*)Cl₃Rh, **2**, and (*o*-Ph)₂PC₆H₄-*t*-CH=CHC₆H₄PPh₂-*o*)Cl₃Ir, **3**. In **2** and **3** the M-Cl bonds trans to chlorine and trans to the olefinic function do not differ significantly in length. This implies that, for both metals, the trans influences of chloride and olefinic ligands are similar. M-Cl distances in both **2** and **3** [means of 2.344 (1) and 2.359 (1) Å, respectively] fall generally within the range of values reported for appropriate M-Cl distances in similar complexes.²⁴ However, the mean M-Cl distance in the rhodium complex **2** is significantly shorter than that in the iridium complex **3** ($\Delta/\sigma \approx 15$). Conversely, the M-C(olefin) distance in **2** [2.238 (2) Å] is significantly longer than that in **3** [2.203 (3) Å, $\Delta/\sigma \approx 10$] while the M-P distances [2.385 (1) Å in **2** and 2.383 (1) Å in **3**] are equal to within experi-

(23) The degree of bend-back may be measured by the dihedral angle between the R₁R₂C and R₃R₄C planes of an olefin R₁R₂C=CR₃R₄ provided there is no large relative twist of the olefinic moiety about the C=C bond direction. This condition is satisfied for **1**.

(24) For example: Ir-Cl = 2.361 Å in *mer*-(PMe₂Ph)₂Cl₃Ir (Aslanov, L.; Mason, R.; Wheeler, A. G.; Whimp, P. O. *J. Chem. Soc., Chem. Commun.* **1970**, 30), Rh-Cl = 2.362 Å in *mer*-(PEt₂Ph)₂Cl₃Rh (Skapski, A. C.; Stephens, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1789), and 2.361 Å in *trans*-(PEt₂)₂(CHNMe₂)-*mer*-Cl₃Rh (Cetinkaya, B.; Lappert, M. F.; McLaughlin, G. M.; Turner, K. *Ibid.* **1974**, 1591).

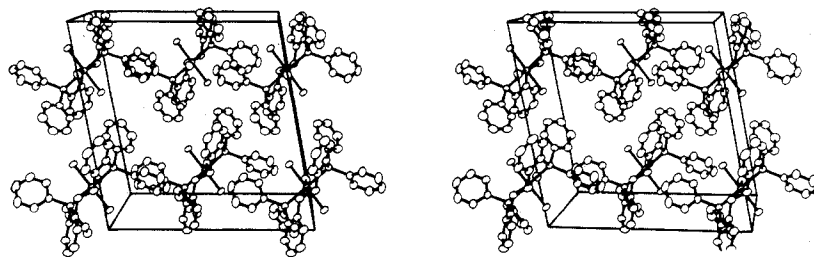


Figure 4. A stereoscopic pair illustrating the unit cell contents for (bdpps) $\text{Cl}_3\text{Ir}^{\text{III}}$ viewed approximately along *b*. The packing for (bdpps) $\text{Cl}_3\text{Rh}^{\text{III}}$ is almost identical.

Table VII

Mean Plane Calculations for (bdpps)CIR^h-CH₂Cl₂ (1)

plane	defined by atoms	dev from the plane, Å							
i	Rh, P(1), P(2)	Rh	0.006	P(1)	0.194	P(2)	0.101	Cl	0.117
	Cl, C(117), C(217)	C(117)	-0.793	C(217)	0.609				
ii	C(111), C(112), C(113)	C(111)	-0.009	C(112)	0.007	C(113)	0.002	C(114)	-0.010
	C(114), C(115), C(116)	C(115)	0.009	C(116)	0.001	P(1)	-0.231	C(111)	0.102
iii	C(211), C(212), C(213)	C(211)	0.000	C(212)	-0.001	C(213)	-0.002	C(214)	0.006
	C(214), C(215), C(216)	C(215)	-0.006	C(216)	0.003	P(2)	0.176	C(217)	0.011
iv	C(112), C(117), C(217)	H(217)	0.057						
v	C(117), C(217), H(217)	C(112)	-0.084						
vi	C(212), C(217), C(117)	H(117)	-0.080						
vii	C(217), C(117), H(117)	C(212)	0.121						
viii	C(112), C(117), H(117)								
ix	C(212), C(217), H(217)								
	C(117), C(217), C(112)	C(117)	-0.196	C(217)	-0.236	C(112)	0.175	C(212)	0.184
x	C(212), H(117), H(217)	H(117)	0.032	H(217)	0.041				
	Rh, C(117), C(217)								
xi									

Dihedral Angles (Deg) between Planes

iv-v = 3.8

vi-vii = 5.4

viii-ix = 55.3

i-xi = 77.8

i-x = 94.1

Angle between the P(1)-P(2) and C(117)-C(217) Vectors: 78.9°

mental error. Since the complexes are isomorphous, the bond length differences cannot be substantially affected by differing inter- and intramolecular interactions. Instead they must reflect, almost exclusively, differences in the primary bonding properties between Rh(III) and Ir(III). In view of the approximate equality of M-P bonds in the two molecules, we conclude that the shortened M-C(olefin) bond in **3** can only result from more facile back-donation of charge by the "heavier" metal atom. Such an effect is consistent with the observation that higher oxidation states are relatively more stable for third row, rather than second row, transition metals. The origin of the smaller difference in the M-Cl distances is, however, altogether less clear.²⁵

M-P distances, like the M-Cl distances, are unexceptional. The Ir-P distance in **3** [2.383 (1) Å] is close to the average values [2.37-2.40 Å²⁶] observed for Ir(III)-P (trans to

phosphine) bonds except where the complex contains hydrido ligands, in which case the P-Ir-P angle deviates substantially from 180° and the Ir-P distance is shorter (ca. 2.34 Å²⁷). The Rh(III)-P distance in **2** [2.385 (1) Å] also compares well with corresponding average values in similar complexes.²⁸

The M-C(olefin) distance in **2** [2.238 (2) Å] is rather longer than the corresponding mean distances in (acac)(H₂O)(C₁₂H₁₂F₆)Rh [2.09 (1) Å²⁹] and [(C₁₁H₈F₆)-ClRh]₄ [2.15 (2) Å³⁰], in which complexes the trifluoromethyl-substituted olefins are parts of strained tridentate chelating ligands. In contrast, the Ir-C(olefin) distance in **3** [2.203 (3) Å] is shorter than the average [2.308 Å] of the two inequivalent distances [2.269 (9) and 2.347 (8) Å] in [1,2-bis(trifluoromethyl)-3-acetyl-1-oxopent-1-enyl][1-(bis(trifluoromethyl)ethylene)-oct-4-enyl]iridium(III).³¹ In the complex [Ph₂P(CH₂)₂-*t*-CH=CH(CH₂)₂PPh₂]₂H₂ClIr¹⁷ the hydride ligand trans to the olefinic function results in a longer average Ir-C(olefin) distance (2.313 Å) than in **3**.

- (25) If the difference in M-Cl distances reflects a difference in metal covalent radii ($r(\text{Rh}) < r(\text{Ir})$), then the equivalence of M-P distances could result from relatively greater metal $d\pi$ /phosphorus $d\pi$ back-bonding in the Ir(III) complex paralleling the greater metal-olefin back-bonding. If, however, the equality of M-P distances reflects an equality of metal covalent radii ($r(\text{Rh}) = r(\text{Ir})$), then there is an implied weakening of Ir-Cl relative to Rh-Cl. This would be consistent with an increase in ionic character of the Ir-Cl bond and a higher positive charge on iridium relative to rhodium. These two rationalizations are indistinguishable on the basis of our data, and, indeed, they are not necessarily mutually independent.
- (26) For example: 2.370 Å in (PPh₃)₃(*p*-MeOC₆H₄-N=N)Cl₂Ir (Bellon, P. L.; Caglio, G.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* 1974, 897), 2.379 Å in (PPh₃)₂(C≡CR)(CH=CHR)Cl(CO)Ir (R = B₁₀C₂H₁₁; Callahan, K. P.; Strouse, C. E.; Layten, S. W.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* 1973, 465), 2.420 Å in (PPh₃)₂(CHF₂)(CO)Cl₂Ir (Schultz, A. J.; McArdle, J. V.; Khare, G. P.; Eisenberg, R. *J. Organomet. Chem.* 1974, 72, 415), and 2.412 Å in (PPh₃)₂(CHF₂)(CO)(CO₂CF₃)ClIr (Schultz, A. J.; Khare, G. P.; Meyer, C. D.; Eisenberg, R. *Inorg. Chem.* 1974, 13, 1019).

- (27) Ir-P and P-Ir-P, respectively, are 2.339 Å and 151.4° in [(PPh₃)₃(CO)H₂Ir]⁺ (Bird, P.; Harrod, J. F.; Than, K. A. *J. Am. Chem. Soc.* 1974, 96, 1222), 2.341 Å and 167.4° in (PPh₃)₂(C₆H₄-N=NPh)HClIr (Van Baar, J. F.; Meij, R.; Olie, K. *Cryst. Struct. Commun.* 1974, 3, 587), 2.286 Å and 153.0° in (PPh₃)₃Ir (Clark, G. R.; Skelton, B. W.; Waters, T. N. *Inorg. Chim. Acta.* 1975, 12, 235), and 2.292 Å and 170.1° in [Ph₂P(CH₂)₂-*t*-CH=CH(CH₂)₂PPh₂]₂H₂ClIr.¹⁷
- (28) For example: 2.370 Å in *trans*-(PEt₃)₂(CHNMe₂)-*mer*-Cl₃Rh (Cetin-kaya, B.; Lappert, M. F.; McLaughlin, G. M.; Turner, K. *J. Chem. Soc., Dalton Trans.* 1974, 1591), 2.389 Å in (P-*n*-Bu₃)₂(P(OMe)₃)Cl₃Rh (Allen, F. H.; Chang, G.; Cheung, K. K.; Lai, T. F.; Lee, L. M.; Pidcock, A. *J. Chem. Soc., Chem. Commun.* 1970, 1297), and 2.398 Å in *mer*-(PPhEt₂)₃Cl₃Rh (Skapski, A. C.; Stephens, F. A. *J. Chem. Soc., Dalton Trans.* 1973, 1789).
- (29) Russell, D. R.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* 1976, 841.
- (30) Evans, J. A.; Kemmitt, R. D. W.; Kimura, B. Y.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* 1972, 509.
- (31) Russell, D. R.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* 1975, 1749.

Table VIII

Mean Plane Calculations for (bdpps)Cl₃Rh^{III} (**2**) and (bdpps)Cl₃Ir^{III} (**3**)

plane	defined by atoms	dev from the plane, ^a Å					
		M	0.000, 0.000		P	-0.044, -0.048	
i	M, ^a P, P, ^b Cl(1)	M	0.000, 0.000		P	-0.044, -0.048	
	C(17), C(17) ^b	C(17)	0.156, 0.172		C(17) ^b	-0.156, -0.172	
	C(11), C(12), C(13)	C(11)	-0.012, -0.020		C(12)	0.006, 0.009	
ii	C(14), C(15), C(16)	C(14)	-0.014, -0.015		C(15)	0.008, 0.004	
		P	-0.233, -0.232		C(17)	0.057, 0.057	
		H(17)	-0.111, -0.098				
iii	C(12), C(17), C(17) ^b	C(12)	-0.182, -0.187		C(17)	0.080, 0.098	
iv	C(17), C(17) ^b , H(17)	C(12) ^b	-0.182, -0.187		C(17) ^b	0.080, 0.098	
v	C(12), C(17), H(17)						
vi	C(12), ^b C(17), ^b H(17) ^b						
vii	C(17)						
viii	C(17), ^b H(17), H(17) ^b						
	M, C(17), C(17) ^b						

Dihedral Angles (Deg) between Planes

iii-iv = 7.1, 6.5

v-vi = 28.0, 33.1

i-viii = 13.2, 14.4

Angle between the P-P and C(17)-C(17)^b Vectors: 14.3 and 15.5°

^a The first given number refers to the Rh(III) complex and the second to the Ir(III) complex. ^b Refers to atoms related to those in Tables III and IV by the operation $-x, y, 1/2 - z$.

The observed shortening of the M-C(olefin) bonds in **3** vis à vis **2**, attributed above to more facile back-donation from Ir(III) than from Rh(III), is accompanied, as expected, by a relative increase in the C=C(olefin) bond length [1.386 (5) Å in **3**; cf. 1.367 (4) Å in **2**] and in the degree of olefin rehybridization (Table VIII).

Comparison of M(I) and M(III) Complexes. A detailed comparison of bond lengths between **1** and **2** is probably not useful because of the differences in metal coordination number and crystal packing. However, two gross features are worthy of comment. First, the degree of back-donation from the metal to the olefinic function, as measured by the Rh-C and C=C bond lengths and the degree of nonplanarity of the olefin, is much greater for Rh(I) than for Rh(III). This would be anticipated on the basis of a larger number of electrons formally associated with the metal in the lower oxidation state. The second important difference is in the orientation of the olefinic bond. In **1** the olefin bond direction is approximately perpendicular to the metal coordination plane (Table VII) whereas in **2** (and in **3**) it is approximately parallel to the equivalent coordination plane (and the P-P vector; see Figure 3). The perpendicular orientation is usually observed in Rh(I)-olefin complexes, but it is of interest to decide whether or not the different orientation in **2** is geometrically or electronically preferred (vide infra).

In all three complexes the phenyl groupings are planar to within experimental error. Deviations of the phosphorus atoms and olefinic carbon atoms from the appropriate planes are contained in Tables VII and VIII. The P-C and C-C(phenyl) bond lengths and the C-C-C(phenyl) bond angles are unexceptional with mean values of 1.814 (8) Å, 1.382 (12) Å and 120.0 (8)° respectively. There are no evident trends in C-C-C angles or C-C lengths that distinguish the *o*-phenylene from the phenyl groupings.

The P-C-C angles of the *o*-phenylene groupings that are internal to the chelate ring are all smaller than the "ideal" value of 120° (vide infra). The C(phenyl)-C-C(olefin) angles do not differ greatly from 120° in **1** but are slightly larger in **2** and **3**. The C(phenyl)-C(olefin) distances (mean 1.502 Å) are not greatly different from the expected value (1.51 Å³²) for a C(sp²)-C(sp²) single bond showing that there is no extended delocalization over the stilbene grouping.

The Bis(diphenylphosphino)stilbene Ligand. The observed internal angles in the tridentate chelating ligand are compared in Figure 5. It is clear that there are some considerable

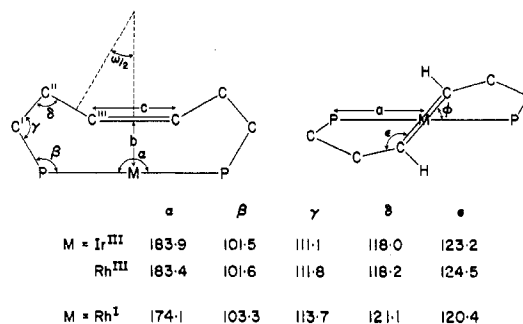


Figure 5. A comparison of internal angles in the tridentate chelate for the three complexes. [The angle α is imprecisely defined in the case of the Rh(I) complex. It is taken as being the projection of the P-Rh-P angle on the mean coordination plane (Table VII).]

distortions from the expected "ideal" angles. Small differences in equivalent angles between **2** and **3** will not be considered further. The bridging part of the ligand is amenable to a simple geometric calculation, the assumptions and parameterization for which are described in ref 33, which allow us to examine how the angles β , γ , and δ (Figure 5) vary as ϕ changes. The results are illustrated in Figure 6. There are two primary conclusions. First, there will always be angular distortions which is merely stating that the chelate ring is strained. Second, there are in each case two values of ϕ at which the distortions in β , γ , and δ are at a minimum. We will refer to these as the high ϕ minimum (HPM) and the low ϕ minimum (LPM).³⁴ The Rh(I) complex exhibits an HPM ($\phi_{\text{obsd}} = 78.9^\circ$) and the M(III) complexes exhibit an LPM [$\phi_{\text{obsd}} = 14.3^\circ$ for M = Rh(III) and $\phi_{\text{obsd}} = 15.5^\circ$ for M = Ir(III)].

(33) The underlying assumption in the calculation is that distorting the bond lengths significantly, except perhaps for the M-P bonds, is a higher energy process than that of distorting bond angles. We assume therefore P-C = 1.82, C-C(phenyl) = 1.39, and C(phenyl)-C(olefin) = 1.51 Å. We further assume that distances b and c (Figure 5) and the angle of bend-back of the olefin (ω) are those observed in the crystal structures, namely, 2.09 Å, 1.38 Å, and 30° for the M(III) complexes and 1.98 Å, 1.44 Å, and 55° for the M(I) complex. Given the distance a and angles α and ϵ we can compute β , γ , and δ (only one angle of which is independent if the atoms P, C', C'', and C''' are coplanar) as a function of ϕ . The calculation at the experimental ϕ value does not give exactly the same values of β , γ , and δ as in the crystal structures primarily because P, C', C'', and C''' are not exactly coplanar.

(34) A simple Dreiding model suggests that a similar situation occurs in [Ph₂P(CH₂)₂-*t*-CH=CH(CH₂)₂PPh₂]₂H₂ClIr^{III}.¹⁷ However, in that complex the constraints imposed by the chelating ligand result in a LPM of ca. 40°.

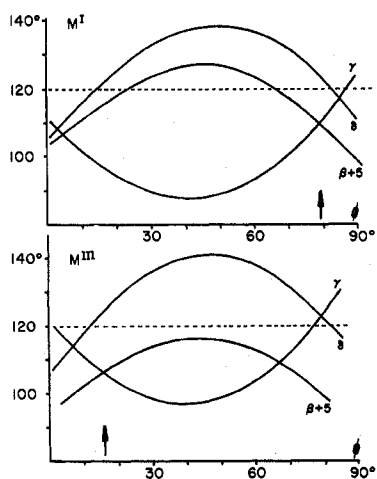


Figure 6. Calculated variations in the angles β , γ , and δ (Figure 5) with changing angle ϕ for the Rh(I) and M(III) ($M = \text{Rh, Ir}$) complexes. The arrows mark the observed values of ϕ for the complexes.

The calculations show that for both M(I) and M(III) complexes the distortions in β , γ , and δ^{35} are smaller at the HPM than at the LPM, so that in principle there is, in each case, a geometric preference for the HPM. Therefore³⁶ we

- (35) The HPM and LPM have been calculated as being at the minimum of the sums of the squares of β , γ , and δ from their ideal values. These were assumed to be 120° for γ and δ and 115° for β . The latter value is somewhat arbitrary. Furthermore, we feel intuitively that distortions in β are less energetically unfavorable than those in γ and δ . Nevertheless, variations in the assumed "ideal" for β and differing modes of calculating the minimum do not alter the qualitative conclusions we have drawn.
- (36) Clearly the phosphine conformation observed in the M(III) complexes would introduce no extra nonbonded interactions in a M(I) complex. The reverse situation is less certain, but placement of two mutually trans chlorine atoms 2.34 Å from the metal along a vector perpendicular to the mean coordination plane of the metal does not introduce severe nonbonded interactions between the phosphine phenyl groups and the extra chlorine atoms.

conclude that the observed LPM in the d^6 M(III) complex is electronically preferred.³⁷

Variations in α and ϵ are also important³⁸ because in the M(I) complex these angles are smaller and in the M(III) complexes larger than their ideal values (180° and ca. 120° , respectively). Further calculations performed by varying the parameters α and ϵ about their observed values show that an increase in either or both reduces distortions in β , γ , and δ at both the HPM and LPM. There is also a concomitant change in the ϕ value of the HPM and LPM. Since the effect of increasing α and/or ϵ in the M(I) complex³⁹ is to relieve chelate ring strain it is pertinent to ask why this does not occur. A likely reason is that the resultant ϕ value at the HPM is then still smaller than the observed value (78.9°). Therefore we conclude that as well as the previously discussed geometric preference for a HPM there is an electronic preference for a ϕ value approaching 90° in the d^8 M(I) complex.

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Registry No. 1, 38904-91-5; 2, 61300-52-5; 3, 59706-98-8.

Supplementary Material Available: Listings of anisotropic atomic thermal parameters, structure factor amplitudes, and data collection details (37 pages). Ordering information is given on any current masthead page.

- (37) A recent LCAO-MO-SCF calculation (Bachmann, C.; Demuyneck, J.; Veillard, A. *J. Am. Chem. Soc.* **1978**, *100*, 2366) on the model d^6 metal complex $\text{trans-Mo}(\text{PH}_3)_4(\text{C}_2\text{H}_4)_2$ suggest that the most stable configuration has the olefinic bond parallel to the P-P vector. This is analogous to the LPM observed in the d^6 M(III) complexes of this work.
- (38) Distortions in β , γ , and δ are relatively insensitive to the variation of a (Figure 5) by ca. 0.1 Å.
- (39) In the M(III) complexes distortions in α and ϵ are balanced against distortions in β , γ , and δ .

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Crystal Structure and Solution Dynamics of the Cyclopropylplatinum(II) Complex (2,3-Bis(methoxycarbonyl)-1-methylcyclopropyl)bis(triphenylphosphine)platinum(II) Tetrafluoroborate

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The crystal structure and dynamic behavior in solution of one of the products of the reaction of *trans*-PtH(acetone)(PPh₃)₂BF₄ and *cis*-dimethyl 1-methylenecyclopropane-2,3-dicarboxylate have been determined. The cyclopropylplatinum(II) complex (2,3-bis(methoxycarbonyl)-1-methylcyclopropyl)bis(triphenylphosphine)platinum(II) tetrafluoroborate crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.513(1)$ Å, $b = 19.247(3)$ Å, $c = 19.874(4)$ Å, $\beta = 92.02(1)^\circ$, and $Z = 4$. The structure was refined with 5382 observations and 224 variables to an R index on F_o of 0.035. The structure confirms the integrity of the cyclopropane ring and shows that the fourth coordination site on the Pt is occupied by one of the ester carbonyls. The compound exhibits dynamic ¹H and ¹³C NMR spectra that are attributed to the rapid dissociation of the coordinated carbonyl.

Introduction

The reactions of methylenecyclopropane derivatives with zero- and divalent complexes of platinum and palladium generally give either (1) η^2 -olefin complexes in which the methylenecyclopropane framework remains intact or (2) η^3 -allyl or but-3-enyl complexes resulting from metal-induced

cyclopropane ring opening.¹⁻⁵ Both of these reaction types have been observed in the reactions of platinum(II) hydrides

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