

Contribution from the Departments of Chemistry, Northwestern University, Evanston, Illinois 60201, and King's College, Strand, London, WC2R 2LS, England

Complexes of the Platinum Metals. 12.¹ *N,N'*-Di-*p*-tolylformamidinato Derivatives of Ruthenium, Osmium, and Iridium. Crystal Structure of *trans*-Bis(triphenylphosphine)carbonyl(*N,N'*-di-*p*-tolylformamidinato)-hydridoruthenium(II)

LEO D. BROWN,^{2a} STEPHEN D. ROBINSON,^{*2b} ARVIND SAHAJPAL,^{2b} and JAMES A. IBERS^{*2a}

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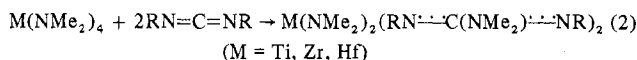
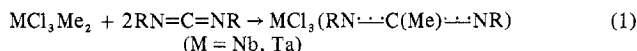
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N,N'-Di-*p*-tolylcarbodiimide (tolN=C=Ntol) (tol = *p*-tolyl) reacts with platinum group metal hydrides to afford products containing the symmetrical *N,N'*-bonded ligand *N,N'*-di-*p*-tolylformamidinato (tolN=CH=Ntol = dtfa). Thus, the hydrides [MHX(CO)(PPh₃)₃] (M = Ru or Os; X = Cl, Br, or OCOCF₃), [MH₂(CO)(PPh₃)₃], [RuH₂(PPh₃)₄] or [OsH₄(PPh₃)₃], [IrHCl₂(PPh₃)₃] (trans chlorides), and *mer*-[IrH₃(PPh₃)₃] yield the complexes [MX(dtfa)(CO)(PPh₃)₂] (two isomers), [MH(dtfa)(CO)(PPh₃)₂], [M(dtfa)₂(PPh₃)₂], [IrCl₂(dtfa)(PPh₃)₂], and [IrH₂(dtfa)(PPh₃)₂], respectively. The structure and stereochemistry of the new complexes have been deduced from ¹H and ³¹P NMR data. In addition, the structure of the complex *trans*-RuH(dtfa)(CO)(PPh₃)₂ has been unambiguously established by x-ray diffraction methods. The compound crystallizes in the monoclinic space group C_{2h}⁶-C₂/c with eight molecules in the unit cell of dimensions *a* = 24.465 (4) Å, *b* = 11.845 (2) Å, *c* = 30.260 (5) Å, β = 98.38 (1)°, and *V* = 8674.9 Å³; ρ_{calcd} = 1.344 and ρ_{obsd} = 1.34 g cm⁻³. A full-matrix least-squares refinement of the structure by standard procedures resulted in an *R* index of 0.063 for the 5805 independent data for which *F*_o² > 3σ(*F*_o²). The coordination about the ruthenium atom is approximately octahedral. The formamidinato ligand is coordinated to the metal atom in a bidentate mode with an N(1)-Ru-N(2) angle of 59.8 (2)° and an N(1)-C(2)-N(2) angle of 114.7 (5)°. The Ru-N(2) bond length is 2.248 (5) Å compared with the Ru-N(1) distance of 2.183 (5) Å. The N-C bond lengths within the formamidinato moiety are equal with N(1)-C(2) and C(2)-N(2) distances of 1.308 (7) and 1.315 (7) Å, respectively. The two tolyl rings are twisted approximately 70° with respect to one another. The position of the hydrido ligand was refined in the structural analysis; the Ru-H distance is 1.58 (7) Å.

Introduction

In preceding papers^{3,4} we have discussed reactions of carbon disulfide and alkyl or aryl isothiocyanates with platinum metal hydrides leading to formation of dithioformato and *N*-alkyl- or *N*-aryltioformamido complexes, respectively. We now report a logical extension of this work, the reaction of *N,N'*-di-*p*-tolylcarbodiimide (tolN=C=Ntol; tol = *p*-tolyl) with the same hydrides, and identify the products as *N,N'*-di-*p*-tolylformamidinato (tolN=CH=Ntol = dtfa) derivatives arising from the "insertion" of the carbodiimide into the metal-hydrogen bonds. The stereochemistry of these complexes and the symmetrical chelate nature of the dtfa ligand have been tentatively established by ¹H and ³¹P NMR, and have been fully confirmed for the complex *trans*-RuH(dtfa)(CO)(PPh₃)₂ by x-ray diffraction methods. Part of this work has been described in a preliminary publication.⁵

Although the coordination chemistry of allenes⁶ and selected heteroallenes, in particular carbon dioxide^{7,8} and carbon disulfide,⁹ has recently been extensively studied, relatively little is known concerning the reactions of *N,N'*-dialkyl- or *N,N'*-diarylcarbodiimides (RN=C=NR, R = alkyl or aryl) with transition metal species. Insertion of carbodiimides into metal-methyl¹⁰ and metal-dimethylamino linkages¹¹ affords acetamidinato and guanidinato derivatives, respectively



In contrast, attempts to insert carbodiimides into the metal-chlorine bonds of PdCl₂(NCPPh)₂ gave only simple N-coordinated substitution products PdCl₂(RN=C=NR)₂.¹² Carbodiimides also apparently function as simple N donors in the complexes PtCl₂(C₂H₄)(RN=C=NR) and RhCl(CO)₂(RN=C=NR) (R = *t*-Bu or *i*-Pr).¹³ The present study affords the first examples of carbodiimide insertion into transition metal-hydrogen linkages leading to formation of formamidinato complexes. However, formamidinato complexes have previously been prepared by treatment of silver or copper carboxylates or chlorides (in the presence of base)

with the corresponding formamidines (RN=CHNHR)¹⁴ and by halide metathesis using lithium formamidates.^{15,16} Products prepared by the latter method include PdCl(RN=CH=NR)(PPh₃)₂ (R = Ph, *p*-C₆H₄Cl, *p*-C₆H₄Me, and *p*-C₆H₄OMe), Pd₂(RN=CH=NR)₄,¹⁵ and PtCl(RN=CH=NR)(PPh₃)₂.¹⁶ Complexes containing the closely related amidinato ligands RN=C(R')=NR include the species Mo₂(PhN=C(Ph)=NPh)₄¹⁷ and Re₂Cl₄(PhN=C(Ph)=NPh)₂¹⁸ prepared by the reaction of *N,N'*-diphenylbenzamidine with Mo(CO)₆ and [N-*i*-Pr₄][Re₂Cl₈], respectively, and the species Mn(RN=C(R')=NR)(CO)₅ and Mn(RN=C(R')=NR)(CO)₄ obtained by thermolysis or decarbonylation of the carbamoyl-type intermediates Mn(CON(R)C(R')=NR)(CO)₄ (R = H, Ph, or *p*-tolyl; R' = Ph or Me).¹⁹ X-ray diffraction methods have been employed to establish the presence of bridging *N,N'*-diphenylbenzamidinato ligands in Mo₂(PhN=C(Ph)=NPh)₄¹⁷ and Re₂Cl₄(PhN=C(Ph)=NPh)₂,¹⁸ and chelate acetamidinato ligands in the complexes TaCl₃(*i*-PrN=C(Me)=N-*i*-Pr)₂²⁰ and TaCl₃Me(C₆H₁₁N=C(Me)=NC₆H₁₁)₂.²¹

The diarylformamidinate (ArN=CH=NAr) and diaryltriazenide (ArN=N=NAr) anions are isoelectronic, and a series of 1,3-diaryltriazenido complexes directly analogous to the compounds discussed herein has previously been reported.²² The crystal and molecular structures of the 1,3-di-*p*-tolyltriazenido complex *trans*-RuH(tolN=N=Ntol)(CO)(PPh₃)₂^{23,24} and its 1,3-di-*p*-tolylformamidinato analogue *trans*-RuH(dtfa)(CO)(PPh₃)₂ are compared below.

Experimental Section

Hydrido complexes were prepared as previously described;²⁵ *N,N'*-di-*p*-tolylcarbodiimide was used as purchased from Aldrich Chemical Co. Reagent grade organic solvents were dried over molecular sieves and degassed before use. The light petroleum used had a boiling range 60–80 °C. Reactions were performed under a dinitrogen atmosphere, but products were worked up in air. Oily products were solidified by dissolving in a minimum volume of dichloromethane, then adding methanol (10 mL) to induce precipitation. Solids were washed successively with methanol and light petroleum and then purified by crystallization from dichloromethane-methanol. Analyses, by the microanalytical laboratory of University College,

Table II. NMR^a and Infrared Data

Complex and stereochemistry	$\tau(\text{CH})^d$	$^4J(\text{PH})$, Hz (cis, trans)	$\tau(\text{Me})$	$\tau(\text{MH})$	$\nu(\text{CO})$, cm^{-1}	$\nu(\text{MH})$, cm^{-1}
[RuCl(dtfa)(CO)(PPh ₃) ₂] (V)	2.26 t	2.65	7.78, 7.84		1920	
[RuBr(dtfa)(CO)(PPh ₃) ₂] (V) ^{b,c}	2.14 t	2.65	7.77, 7.84		1920	
[Ru(OCOCF ₃)(dtfa)(CO)(PPh ₃) ₂] (V)	Masked		7.75		1948	
[RuH(dtfa)(CO)(PPh ₃) ₂] (VI)	Masked		7.74, 7.90	23.37 t, 20	1930	2119
[Ru(dtfa) ₂ (PPh ₃) ₂] (VII)	1.85 br		7.82, 7.90			
[OsCl(dtfa)(CO)(PPh ₃) ₂] (IVa) ^b	1.20	2.35, 6.5	7.73, 7.75		1940	
[OsBr(dtfa)(CO)(PPh ₃) ₂] (IVa) ^b	1.25	2.35, 6.5	7.74, 7.76		1940	
[Os(OCOCF ₃)(dtfa)(CO)(PPh ₃) ₂] (IVa)	0.92	1.5, 6.2	7.76		1948	
[OsCl(dtfa)(CO)(PPh ₃) ₂] (V) ^b	1.39 t	2.5	7.80, 7.84		1915	
[OsBr(dtfa)(CO)(PPh ₃) ₂] (V)	1.37 t	~2.0	7.79, 7.83		1915	
[OsH(dtfa)(CO)(PPh ₃) ₂] (VI)	1.38 br		7.74, 7.90	24.58 t, 17.3	1915	2100
[Os(dtfa) ₂ (PPh ₃) ₂] (VII)	0.76 br		7.79, 7.84			
[IrCl ₂ (dtfa)(PPh ₃) ₂] (VIII) ^c	0.68 t	1.75	7.85			
[IrH ₂ (dtfa)(PPh ₃) ₂] (X)	0.97 br		7.85	32.76 t, 17		2185

^a All NMR spectra taken in CDCl₃ unless otherwise noted. ^b Spectrum taken in CD₂Cl₂ solution. ^c Solvated with CH₂Cl₂ (0.25 mol) τ 4.72. ^d d = doublet, t = triplet, br = broad.

Table III. ³¹P NMR Data^a

Complex and stereochemistry	δ , ppm	$^2J(\text{PP}')$, Hz
[RuCl(dtfa)(CO)(PPh ₃) ₂] (V)	29.38 s	
[Ru(OCOCF ₃)(dtfa)(CO)(PPh ₃) ₂] (V)	35.5 s	
[Ru(dtfa) ₂ (PPh ₃) ₂] (VII)	52.8 s	
[OsCl(dtfa)(CO)(PPh ₃) ₂] (IVa)	5.55 } AB pattern	11.0
	0.16 }	
[OsBr(dtfa)(CO)(PPh ₃) ₂] (IVa)	4.71 } AB pattern	9.75
	-1.85 }	
[Os(OCOCF ₃)(dtfa)(CO)(PPh ₃) ₂] (IVa)	2.8 } AB pattern	11.0
	0.87 }	
[OsCl(dtfa)(CO)(PPh ₃) ₂] (V)	0.29 s	

^a Spectra taken in CDCl₃ and referenced to external H₃PO₄ in the sense that positive values are to low field. All spectra proton decoupled. ^b Spectrum taken in CD₂Cl₂; other conditions as above.

London, and melting points, taken in sealed tubes under dinitrogen, are given in Table I.²⁶

Proton and phosphorus-31 NMR spectra were obtained at 90 and 36.43 MHz, respectively, using a Bruker HFX90 NMR spectrometer. Infrared spectra were run as Nujol mulls on a Perkin-Elmer 457 grating spectrometer. Spectroscopic data are recorded in Tables II and III.

Preparations. Bis(triphenylphosphine)carbonyl(*N,N*-di-*p*-tolylformamidinato)chlororuthenium(II). *N,N'*-Di-*p*-tolylcarbodiimide (0.1 g) and [RuHCl(CO)(PPh₃)₃] (0.4 g) in benzene (20 mL) were heated under reflux for 90 min. The dark yellow-green solution was cooled to room temperature, filtered, concentrated under reduced pressure, and then diluted with methanol (10 mL) to precipitate a bright yellow solid. This was filtered and purified as described above to yield bright yellow crystals (83%). **Bis(triphenylphosphine)carbonyl(*N,N'*-di-*p*-tolylformamidinato)bromoruthenium(II)-dichloromethane (4/1)** was similarly prepared as bright yellow crystals (87%).

Bis(triphenylphosphine)carbonyl(*N,N'*-di-*p*-tolylformamidinato)-(trifluoroacetato)ruthenium(II). A solution of *N,N'*-di-*p*-tolylcarbodiimide (0.1 g) and [RuH(OCOCF₃)(CO)(PPh₃)₂] (0.4 g) in benzene (20 mL) was heated under reflux for ca. 1 h. The yellow-green solution was cooled to ambient temperature, then filtered and concentrated under reduced pressure. The resultant oil was solidified, purified, and crystallized as described above to yield bright yellow crystals (65%).

Bis(triphenylphosphine)carbonyl(*N,N'*-di-*p*-tolylformamidinato)-hydridoruthenium(II). A solution of [RuH₂(CO)(PPh₃)₃] (0.5 g) and *N,N'*-di-*p*-tolylcarbodiimide (0.1 g) in toluene (20 mL) was heated under reflux for 5 h. The dark yellow-brown solution was cooled to ambient temperature and filtered. The filtrate was then concentrated under reduced pressure to yield an oil which was crystallized and purified as described above to afford the required product as shiny yellow needles (92%).

Bis(triphenylphosphine)bis(*N,N'*-di-*p*-tolylformamidinato)ruthenium(II). A solution of *N,N'*-di-*p*-tolylcarbodiimide (0.1 g) and [RuH₂(PPh₃)₄] (0.3 g) in benzene (20 mL) was heated under reflux

for 6 h. The yellow-brown solution was then cooled to ambient temperature, filtered, and concentrated to an oil under reduced pressure. The oil was crystallized and purified as described above to yield mustard yellow microcrystals (58%).

Bis(triphenylphosphine)carbonyl(*N,N'*-di-*p*-tolylformamidinato)-chloroosmium(II) (Stereochemistry IVa). A mixture of [OsHCl(CO)(PPh₃)₃] (0.4 g) and *N,N'*-di-*p*-tolylcarbodiimide (0.15 g) in benzene (20 mL) was heated under reflux for ca. 30 h. The pale lime-yellow solution was cooled to ambient temperature, filtered, concentrated under reduced pressure, and then diluted with methanol (10 mL) to precipitate a pale yellow solid. The precipitate was filtered off, then purified and crystallized as described above to yield pale yellow microcrystals (71%).

Bis(triphenylphosphine)carbonyl(*di-p*-tolylformamidinato)-bromoosmium(II) (stereochemistry IVa) was similarly prepared as pale yellow crystals (71%).

Bis(triphenylphosphine)carbonyl(*N,N'*-di-*p*-tolylformamidinato)-(trifluoroacetato)osmium(II). A solution of *N,N'*-di-*p*-tolylcarbodiimide (0.1 g) and [OsH(OCOCF₃)(CO)(PPh₃)₂] (0.35 g) in benzene (20 mL) was heated under reflux for 4 h. The bright yellow solution was then cooled to ambient temperature, filtered, and concentrated to an oil under reduced pressure. The oil was dissolved in a minimum volume of dichloromethane and then diluted with light petroleum (10 mL) to precipitate the required product as a pale yellow solid. The precipitate was filtered off, washed thoroughly with light petroleum, and recrystallized from dichloromethane-light petroleum as pale yellow crystals (68%).

Bis(triphenylphosphine)carbonyl(*N,N'*-di-*p*-tolylformamidinato)-chloroosmium(II) (Stereochemistry V). A mixture of *N,N'*-di-*p*-tolylcarbodiimide (0.15 g) and [OsHCl(CO)(PPh₃)₃] (0.4 g) in toluene (20 mL) was heated under reflux for ca. 24 h. The lime-yellow solution was then cooled to ambient temperature, filtered, and concentrated to an oil under reduced pressure. The oil was solidified, purified, and crystallized as described above to yield bright yellow crystals (80%). **Bis(triphenylphosphine)carbonyl(*di-p*-tolylformamidinato)bromoosmium(II) (stereochemistry V)** was similarly prepared as pale yellow crystals (71%).

Bis(triphenylphosphine)carbonyl(*N,N'*-di-*p*-tolylformamidinato)-hydridoosmium(II). A mixture of *N,N'*-di-*p*-tolylcarbodiimide (0.1 g) and [OsH₂(CO)(PPh₃)₃] (0.4 g) in toluene (20 mL) was heated under reflux for 9 h. The lime-green solution was then cooled to ambient temperature, filtered, and concentrated to an oil under reduced pressure. The oil was crystallized and purified as described above to yield pale yellow microcrystals (68%).

Bis(triphenylphosphine)bis(*N,N'*-di-*p*-tolylformamidinato)osmium(II). A mixture of *N,N'*-di-*p*-tolylcarbodiimide (0.1 g) and [OsH₄(PPh₃)₃] (0.4 g) in toluene (20 mL) was heated under reflux for ca. 20 h. The resultant dark yellow-green solution was cooled to ambient temperature, filtered, and then concentrated to an oil under reduced pressure. The oil was crystallized and purified as described above to yield the required product as mustard yellow microcrystals (59%).

Bis(triphenylphosphine)bis(*N,N'*-di-*p*-tolylformamidinato)dichloro-iridium(III)-Dichloromethane (4/1). A mixture of *trans*-tris(triphenylphosphine)hydridodichloro-iridium (0.4 g) and *N,N'*-di-*p*-

Table IV. Crystal Data for *trans*-RuH(dtfa)(CO)(PPh₃)₂

Mol formula	C ₅₂ H ₄₆ N ₂ OP ₂ Ru	Space group	C _{2h} ⁶ -C2/c
Mol wt	877.98	Z	8
Cell constants ^a	<i>a</i> = 24.465 (4) Å <i>b</i> = 11.845 (2) Å <i>c</i> = 30.260 (5) Å β = 98.38 (1)° <i>V</i> = 8674.9 Å ³	Density	1.344 g cm ⁻³ (calcd); 1.34 g cm ⁻³ (obsd)
		Crystal dimensions	0.114 × 0.657 × 0.176 mm
		Crystal vol	6.03 × 10 ⁻³ mm ³
		Abs coeff, μ ^a	39.9 cm ⁻¹

^a Cu Kα₁ (λ 1.540 562 Å) at 24 °C ambient temperature.

tolylcarbodiimide (0.1 g) in toluene (20 mL) was heated under reflux for 6 h. The yellow-brown solution was cooled to ambient temperature, filtered, and then concentrated to an oil under reduced pressure. The oil was crystallized and purified as above to yield the product as yellow crystals (62%).

Bis(triphenylphosphine)(*N,N'*-di-*p*-tolylformamidinato)dihydroiridium(III). *mer*-Tris(triphenylphosphine)trihydroiridium (0.5 g) and *N,N'*-di-*p*-tolylcarbodiimide (0.2 g) were heated together in toluene (20 mL) under reflux for 12.5 h. The yellow-brown solution was cooled to ambient temperature, filtered, and then concentrated to an oil under reduced pressure. The oil was dissolved in a minimum volume of acetone and then diluted with methanol (10 mL) to precipitate a pale yellow solid. The precipitate was filtered off, washed successively with small volumes (ca. 5 mL) of methanol and light petroleum, and then recrystallized from acetone-methanol as pale yellow microcrystals (60%).

X-Ray Data Collection. Precession and Weissenberg photographs revealed that the yellow crystals of *trans*-[RuH(dtfa)(CO)(PPh₃)₂] belong to the monoclinic system in space group C_s⁴-Cc or C_{2h}⁶-C2/c. As ultimately confirmed by the solution of the structure, the latter centrosymmetric group is correct. The crystal used for intensity measurements was mounted on a glass fiber approximately along the crystallographic *b* axis. The five faces of the wedge-shaped needle were indexed as 10 $\bar{1}$, 100, 001, 0 $\bar{1}$ 1, and 01 $\bar{1}$. The lattice constants were determined by a least-squares analysis²⁷ of the angle settings of 18 hand-centered reflections on a Picker FACS-I diffractometer (λ(Cu Kα₁) 1.540 562 Å) in the range 65° > 2θ > 55°. The refined cell constants and other relevant crystal data are given in Table IV.

Intensity data were measured in the θ-2θ scan mode on the Picker FACS-I diffractometer using prefiltered Cu Kα radiation at a takeoff angle of 4.0°. The counter was positioned 32 cm from the crystal with an aperture 4.0-mm high and 3.3-mm wide. The reflections were scanned at 2°/min from 0.75° below the Kα₁ peak to 0.75° above the Kα₂ peak. Stationary-crystal, stationary-counter background counts of 10 s each were taken at the beginning and end of each scan.²⁸ Copper foil attenuators were automatically inserted if the counting rate approached 7000 counts/s. Intensity data for +*h*, -*k*, ±*l* were collected out to 2θ = 125°. During the data collection the intensities of six standard reflections were measured after every 100 reflections. These standards showed no significant variations throughout the data collection.

The intensity data were processed as described previously²⁷ with the parameter *p* chosen as 0.04. Of the 7521 unique data collected, 5805 independent reflections were found with significant intensity (*I*_o > 3σ(*I*_o)) and were used in the subsequent solution and refinement of the structure.

Solution and Refinement of the Structure. The ruthenium atom and both phosphorus atoms were located from a Patterson synthesis. A structure factor calculation²⁹ of these three atoms followed by a Fourier synthesis located all of the remaining 55 nonhydrogen atoms. In the ensuing full-matrix least-squares refinements, the function minimized is ∑w(|F_o| - |F_c|)², where |F_o| and |F_c| are the observed and calculated structure amplitudes and w = 4F_o²/σ²(F_o²). Atomic scattering factors and the anomalous dispersion terms were taken from the well-known sources.³⁰ The carbon atoms of the two tolyl and six phenyl rings in the structure were refined as rigid groups³¹ with individual isotropic thermal parameters (*D*_{6h} symmetry, C-C distance = 1.395 Å). With all of the nonhydrogen atoms included with isotropic thermal parameters, the structure refined to *R* = 0.093 and *R*_w = 0.125 where *R* = ∑(|F_o| - |F_c|)/∑|F_o| and *R*_w = (∑w(|F_o| - |F_c|)²/∑wF_o²)^{1/2}.

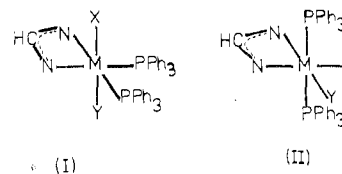
Before proceeding any further an absorption correction was applied to the intensity data. The transmission factors ranged from 0.512

to 0.745. In the subsequent least-squares cycle the ten nongroup atoms were refined anisotropically. In the resulting difference Fourier map all of the hydrogen atoms, including the central hydrogen atom of the dtfa group, were easily located. In addition, the hydrido ligand coordinated to the ruthenium atom was found. In the final least-squares refinements the positional and isotropic thermal parameters of the hydrido ligand were varied. All of the carbon-bonded hydrogen atoms were included in the final calculations as a fixed contribution. The positions of the phenyl hydrogen atoms were uniquely determined from the phenyl carbon atom positions assuming ideal geometry and a C-H distance of 0.95 Å. The six methyl hydrogen atoms were ideally located by a least-squares fit based on the positions of the peaks found in the difference Fourier map. The hydrogen atom bonded to the formamidinato carbon atom was also ideally placed (C-H = 0.95 Å) based on the difference Fourier peak position. Each of the 45 hydrogen atoms was assigned an isotropic thermal parameter 1 Å² greater than the carbon atom to which it is attached. After an additional anisotropic least-squares cycle with the hydrogen contribution, agreement indices of *R* = 0.066 and *R*_w = 0.089 were obtained. On the difference Fourier map virtually all of the significant residual peaks (average peak height ≈ 0.6 e Å⁻³) were close to the isotropically refined carbon atoms of the rigid groups and can be attributed to significant librational motion of the rings not accounted for by the isotropic model. A similar observation was made earlier in the structure of the 1,3-di-*p*-tolyltriazenido analogue of *trans*-[RuH(dtfa)(CO)(PPh₃)₂].²⁴ In order to take the librational motion of the rings into account, the individual group atoms of the triazenido structure were allowed to refine anisotropically. The limited value of such an elaborate model, as discussed previously,²⁴ does not justify its use in the present structure. Thus, the final full-matrix least-squares cycle (5805 independent observations, 192 variables) with individual isotropic thermal parameters for the group atoms resulted in agreement indices *R* = 0.063 and *R*_w = 0.085. The error in an observation of unit weight is 2.78 electrons. The largest peaks in the final difference Fourier synthesis are approximately 0.70 (4) e Å⁻³ (equivalent to 20% the height of a carbon atom); as noted earlier these peaks are associated with the group atoms. Of the 1553 unobserved reflections, 20 were found to have |F_o² - F_c²| > 5σ(F_o²).

The final positional and thermal parameters for the nongroup atoms along with their estimated standard deviations are given in Table V. Table VI lists the derived parameters for the atoms belonging to the eight rigid groups. The root-mean-square amplitudes of vibration for the anisotropic atoms are given in Table VII.²⁶ Table VIII gives the idealized positions of the hydrogen atoms.²⁶ A listing of the 10|F_o| vs. 10|F_c| is also available.²⁶

Results and Discussion

As in the preceding papers,^{3,4} the determination of the structure and stereochemistry of the products described has been achieved primarily using ¹H and ³¹P NMR methods. The central proton of the *N,N'*-di-*p*-tolylformamidinato ligand (dtfa), like those in the related *N*-alkyl- or *N*-arylthioformamido and dithioformato ligands, is highly deshielded and resonates at low field (ca. τ 0.68-2.26); moreover, coupling of this proton to the phosphorus atoms of coordinated phosphine ligands [⁴*J*(PH)_{trans} = ca. 6.5 Hz; ⁴*J*(PH)_{cis} = ca. 1.5-2.5 Hz] provides valuable stereochemical and structural information. In particular, equivalent coupling of the central proton to two *trans* phosphorus nuclei (stereochemistry I)



establishes the intrinsic twofold symmetry of the formamidinato ligand in the complexes under discussion.³²

Similarly equivalent coupling of the central formamidinato proton to the phosphorus nuclei of a pair of mutually *trans* phosphine ligands (stereochemistry II) establishes that the formamidinato ligand is bound in chelate fashion and not as a π-diazaallyl ligand. Nonequivalence of the *p*-tolyl groups

Table V. Positional and Thermal Parameters for the Nongroup Atoms of *trans*-RuH(dtfa)(CO)(PPh₃)₂

ATOM	x ^A	y	z	B ^B ₁₁	B ^B ₂₂	B ^B ₃₃	B ^B ₁₂	B ^B ₁₃	B ^B ₂₃
Ru	0.364525(17)	0.401089(35)	0.626472(13)	15.77(9)	53.40(37)	9.15(6)	0.30(14)	2.92(5)	0.25(10)
P(1)	0.366809(59)	0.20244(12)	0.630727(45)	16.41(27)	56.7(11)	9.72(17)	0.58(44)	2.35(17)	0.11(33)
P(2)	0.372051(62)	0.65006(12)	0.623309(46)	18.97(30)	56.8(11)	10.25(17)	1.50(47)	4.51(18)	1.43(35)
C(1)	0.37735(27)	0.38727(55)	0.56962(22)	23.5(13)	65.4(57)	13.29(83)	0.6(22)	5.66(83)	-0.7(17)
O(1)	0.38601(24)	0.37737(43)	0.53303(15)	39.5(15)	120.1(51)	11.60(62)	-11.1(21)	8.81(75)	-7.6(14)
N(1)	0.34053(20)	0.42219(39)	0.69269(15)	18.13(97)	62.5(40)	8.46(55)	1.5(15)	2.93(58)	0.2(12)
N(2)	0.27475(20)	0.40379(41)	0.63488(15)	16.55(92)	70.5(43)	9.36(57)	-1.5(16)	2.42(58)	0.9(13)
C(2)	0.28753(25)	0.41675(48)	0.67831(18)	18.3(12)	61.6(49)	9.88(69)	1.4(19)	3.40(72)	1.4(14)
C(3)	0.41823(43)	0.46369(82)	0.87999(25)	49.6(28)	140.0(95)	11.44(95)	2.0(43)	-2.3(13)	1.3(25)
C(4)	0.06205(31)	0.27062(76)	0.54402(27)	20.1(15)	131.9(90)	17.9(11)	-0.5(30)	-2.0(11)	-15.0(27)
H(1)	0.4295(27)	0.4101(50)	0.6310(21)	4.3(16)					

^A ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. ^B THE FORM OF THE ANISOTROPIC THERMAL ELIPSOID IS: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS $\times 10^4$.

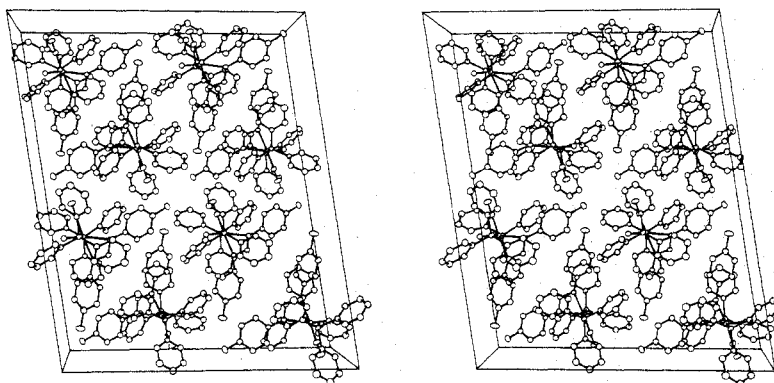


Figure 1. A stereoscopic drawing of the unit cell of *trans*-RuH(dtfa)(CO)(PPh₃)₂. The *y* axis is perpendicular to the plane of the paper going away from the reader, the *z* axis is vertical, and the *x* axis is horizontal and to the right. For the sake of clarity the hydrogen atoms have been omitted from this figure and those that follow. The thermal ellipsoids are drawn at the 20% probability level.

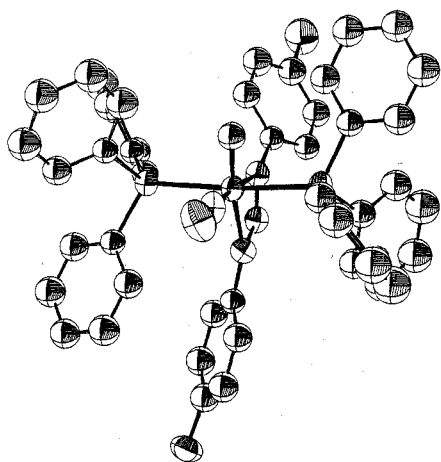


Figure 2. An overall view of the *trans*-RuH(dtfa)(CO)(PPh₃)₂ complex. In this and the following drawing the atoms are shown at the 50% probability contour of thermal motion.

(¹H NMR Me and C₆H₄ resonances) can be taken to indicate that the chelate dtfa ligand is in an asymmetric environment (stereochemistry II). However, the converse is not always true; several complexes containing dtfa ligands *trans* to a nonequivalent ligand pair do not show resolvable differences in the resonances of the two *p*-tolyl groups. A similar phenomenon was observed¹⁹ in the ¹H NMR spectra of the complex Mn(CON(R)≡C(R')≡NR)(CO)₄ (R = *p*-tolyl). Phosphorus-31 NMR data provide valuable confirmatory evidence concerning stereochemistry. Finally, the nature of the formamidinato ligand in the complex RuH(dtfa)(CO)(PPh₃)₂ has been fully established by x-ray diffraction methods. The structural results confirm the stereochemistry proposed from

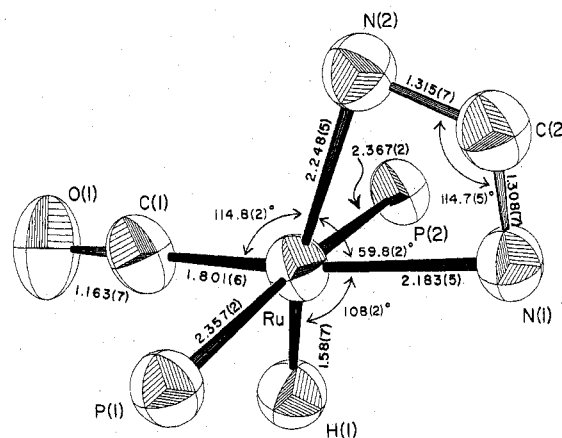


Figure 3. A view of the coordination geometry about the ruthenium atom.

the interpretation of the NMR data.

Description and Discussion of the Structure. The overall structure of the *trans*-RuH(dtfa)(CO)(PPh₃)₂ complex is readily apparent in the stereoscopic drawing of the unit cell as shown in Figure 1. The structure consists solely of monomeric units of the six-coordinate ruthenium complex (see Figure 2). The two *trans* triphenylphosphine ligands have a P(1)-Ru-P(2) angle of 174.24(5)°; the two Ru-P bond distances average 2.362(2) Å. The complex is approximately octahedral, as predicted. The equatorial plane consisting of the hydrido, carbonyl, and the bidentate dtfa ligands exhibits some distortion from ideal octahedral geometry. This is particularly evident in the small N(1)-Ru-N(2) angle of 59.8(2)°, as illustrated in the view of the inner-coordination sphere of the ruthenium atom (see Figure 3). The hydrido ligand

Table VI. Derived Parameters for the Rigid Group Atoms of *trans*-RuH(dtfa)(CO)(PPh₃)₂

ATOM	X	Y	Z	B ₁ A ²	ATOM	X	Y	Z	B ₁ A ²
C(11)	0.36061(15)	0.44037(34)	0.738489(94)	3.65(10)	C(51)	0.37320(16)	0.13766(35)	0.68651(11)	3.65(10)
C(12)	0.40759(15)	0.38091(34)	0.75715(13)	4.67(12)	C(52)	0.32765(13)	0.14352(36)	0.70930(13)	4.47(12)
C(13)	0.42629(15)	0.38661(38)	0.80285(14)	5.55(18)	C(53)	0.33070(16)	0.09753(40)	0.75202(13)	5.26(13)
C(14)	0.39802(18)	0.45578(40)	0.829901(96)	5.27(14)	C(54)	0.37930(20)	0.04567(42)	0.77197(12)	6.52(17)
C(15)	0.35105(17)	0.51525(35)	0.81124(12)	4.94(13)	C(55)	0.42485(16)	0.03981(44)	0.74919(16)	7.37(19)
C(16)	0.33235(14)	0.50754(32)	0.76554(12)	4.21(11)	C(56)	0.42180(14)	0.08581(41)	0.70646(15)	5.65(16)
C(21)	0.22002(13)	0.37779(33)	0.61408(12)	3.62(10)	C(61)	0.31903(16)	0.67579(37)	0.64887(14)	4.54(12)
C(22)	0.18400(16)	0.31527(35)	0.636230(96)	4.82(13)	C(62)	0.33252(15)	0.74391(42)	0.68649(15)	5.61(16)
C(23)	0.13255(15)	0.28282(35)	0.61373(13)	5.28(13)	C(63)	0.29076(22)	0.79446(41)	0.70642(14)	7.23(20)
C(24)	0.11710(13)	0.31289(37)	0.56908(13)	4.97(13)	C(64)	0.23550(19)	0.77690(44)	0.68874(18)	7.18(20)
C(25)	0.15312(16)	0.37540(37)	0.546934(97)	5.20(13)	C(65)	0.22201(14)	0.70878(45)	0.65112(17)	6.88(19)
C(26)	0.20459(15)	0.40785(34)	0.56943(12)	4.87(12)	C(66)	0.26377(18)	0.65823(38)	0.63119(13)	5.28(14)
C(31)	0.42432(15)	0.13901(34)	0.60613(13)	3.61(10)	C(71)	0.43621(14)	0.66543(33)	0.65034(13)	3.96(11)
C(32)	0.41630(14)	0.04760(35)	0.57683(14)	4.60(13)	C(72)	0.44769(16)	0.77739(33)	0.64072(13)	5.22(14)
C(33)	0.46088(19)	0.00257(33)	0.55879(14)	5.84(16)	C(73)	0.49599(19)	0.82843(27)	0.66169(15)	5.75(15)
C(34)	0.51343(16)	0.04895(41)	0.57004(16)	5.86(15)	C(74)	0.53282(15)	0.76752(36)	0.69229(15)	5.33(14)
C(35)	0.52151(14)	0.14035(41)	0.59934(16)	5.89(17)	C(75)	0.52134(16)	0.65556(35)	0.70191(13)	5.37(14)
C(36)	0.47692(18)	0.18539(33)	0.61738(14)	5.58(14)	C(76)	0.47304(17)	0.60451(27)	0.66093(14)	4.84(13)
C(41)	0.30672(14)	0.12707(32)	0.60125(12)	3.66(10)	C(81)	0.36866(17)	0.66385(36)	0.56738(11)	4.13(11)
C(42)	0.28917(17)	0.02245(33)	0.61502(12)	4.96(14)	C(82)	0.41132(16)	0.63556(36)	0.54326(14)	4.99(13)
C(43)	0.24353(18)	-0.03066(29)	0.59065(15)	5.61(15)	C(83)	0.41287(17)	0.68569(42)	0.50151(14)	5.84(16)
C(44)	0.21545(15)	0.02056(36)	0.55249(14)	5.18(15)	C(84)	0.37177(21)	0.76151(42)	0.48388(12)	6.49(16)
C(45)	0.23303(17)	0.12548(36)	0.53871(12)	5.41(14)	C(85)	0.32911(18)	0.78850(39)	0.50799(16)	7.12(19)
C(46)	0.27864(17)	0.17858(28)	0.56309(13)	4.75(13)	C(86)	0.32756(16)	0.73967(40)	0.54974(15)	5.41(14)

RIGID GROUP PARAMETERS

GROUP	X ^A _C	Y ^A _C	Z ^A _C	DELTA ^B	EPSILON	ETA
PH1	0.37932(11)	0.44808(23)	0.784195(92)	0.8817(28)	-2.9237(22)	-1.8305(27)
PH2	0.16856(11)	0.34534(22)	0.591582(90)	-0.4262(47)	2.0926(24)	0.7968(48)
PH3	0.46890(13)	0.09398(25)	0.588084(95)	-0.7323(28)	-2.7100(26)	2.5515(30)
PH4	0.26109(11)	0.07396(24)	0.576869(92)	0.1369(31)	2.4538(27)	0.5626(33)
PH5	0.37625(12)	0.09167(24)	0.729243(93)	-1.8622(30)	2.9662(24)	-1.9379(28)
PH6	0.27727(14)	0.72634(26)	0.66881(11)	2.1185(36)	2.5092(29)	-2.4095(37)
PH7	0.48452(12)	0.71647(25)	0.671311(90)	-2.8505(28)	-2.6566(28)	-0.3840(30)
PH8	0.37022(13)	0.71268(26)	0.52523(10)	1.0299(30)	-2.9353(25)	1.9491(29)

^AX_C, Y_C, AND Z_C ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. ^BTHE RIGID GROUP ORIENTATION ANGLES DELTA, EP-SILON, AND ETA (RADIANS) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERO, ACTA CRYSTALLOGR., 18, 511(1965).

Table IX. Interatomic Distances (Å) and Angles (deg) in *trans*-RuH(dtfa)(CO)(PPh₃)₂

Distances			
Ru-P(1)	2.357(2)	P(2)-C(71)	1.833(4)
Ru-P(2)	2.367(2)	P(2)-C(81)	1.844(4)
Ru-N(1)	2.183(5)	N(1)-C(11)	1.418(5)
Ru-N(2)	2.248(5)	N(2)-C(21)	1.428(6)
Ru-C(1)	1.801(6)	N(1)-C(2)	1.308(7)
Ru-H(1)	1.58(7)	N(2)-C(2)	1.315(7)
P(1)-C(31)	1.845(4)	C(1)-O(1)	1.163(7)
P(1)-C(41)	1.836(4)	C(3)-C(14)	1.527(8)
P(1)-C(51)	1.840(4)	C(4)-C(24)	1.530(8)
P(2)-C(61)	1.838(5)		
Angles			
P(1)-Ru-P(2)	174.24(5)	C(31)-P(1)-C(41)	102.1(2)
P(1)-Ru-N(1)	94.1(1)	C(31)-P(1)-C(51)	103.4(2)
P(1)-Ru-N(2)	91.4(1)	C(41)-P(1)-C(51)	101.4(2)
P(1)-Ru-C(1)	87.4(2)	Ru-P(2)-C(61)	113.9(2)
P(1)-Ru-H(1)	93(2)	Ru-P(2)-C(71)	118.0(1)
P(2)-Ru-N(1)	87.5(1)	Ru-P(2)-C(81)	116.9(1)
P(2)-Ru-N(2)	94.2(1)	C(61)-P(2)-C(71)	102.5(2)
P(2)-Ru-C(1)	91.5(2)	C(61)-P(2)-C(81)	104.3(2)
P(2)-Ru-H(1)	82(2)	C(71)-P(2)-C(81)	99.1(2)
N(1)-Ru-N(2)	59.8(2)	Ru-N(1)-C(2)	94.3(3)
N(1)-Ru-C(1)	174.3(2)	Ru-N(1)-C(11)	144.4(3)
N(1)-Ru-H(1)	108(2)	C(11)-N(1)-C(2)	121.2(5)
N(2)-Ru-C(1)	114.8(2)	N(1)-C(2)-N(2)	114.7(5)
N(2)-Ru-H(1)	168(2)	Ru-N(2)-C(2)	91.2(4)
C(1)-Ru-H(1)	77(2)	Ru-N(2)-C(21)	144.7(3)
Ru-P(1)-C(31)	113.5(1)	C(21)-N(2)-C(2)	122.5(5)
Ru-P(1)-C(41)	116.6(1)	Ru-C(1)-O(1)	179.3(6)
Ru-P(1)-C(51)	117.7(1)		

is 1.58(7) Å from the metal atom. The carbonyl ligand is as expected with a Ru-C(1) distance of 1.801(6) Å and a

virtually linear Ru-C(1)-O(1) angle of 179.3(6)°. A listing of important bond distances and angles is given in Table IX.

The four-membered Ru-N(1)-C(2)-N(2) ring is planar with equivalent N-C bond distances of 1.308(7) and 1.315(7) Å (indicative of π-delocalization within the amidinato moiety). Surprisingly, the two tolyl rings are not coplanar with the amidinato moiety. As illustrated in Figure 2 and from the least-squares plane data tabulated in Table X, each of the two tolyl rings is twisted approximately 36° from the plane of the Ru-N(1)-C(2)-N(2) ring. In addition, the two tolyl rings are twisted approximately 70° from each other. This observation is in marked contrast to the virtual planarity of the entire 1,3-di-*p*-tolyltriazenido (dtf) ligand in the analogous *trans*-RuH(dtt)(CO)(PPh₃)₂ structure.²⁴ A possible explanation of this difference lies in the packing arrangements of the two complexes. The dominant feature of the packing, as shown in Figures 1 and 2, is the arrangement of the phenyl rings of the two *trans* phosphine ligands. In the formamidinato structure reported here, these phenyl groups are in a staggered conformation (this is clearly seen in Figure 1 in which the view is down the P-Ru-P direction). In contrast, the phenyl rings of the *trans* phosphines in the triazenido structure are nearly eclipsed.²⁴ This change in the overall packing arrangement has apparently favored a change in the conformation of the tolyl rings. As noted earlier,³³ the energy differences between these various ring conformations should be relatively small.

The very significant difference between the Ru-N(1) and Ru-N(2) bond lengths (2.183(5) and 2.248(5) Å, respectively) is indicative of a significant trans-effect lengthening by the hydrido ligand opposite to atom N(2). A similar

Table X. Selected Weighted Least-Squares Planes

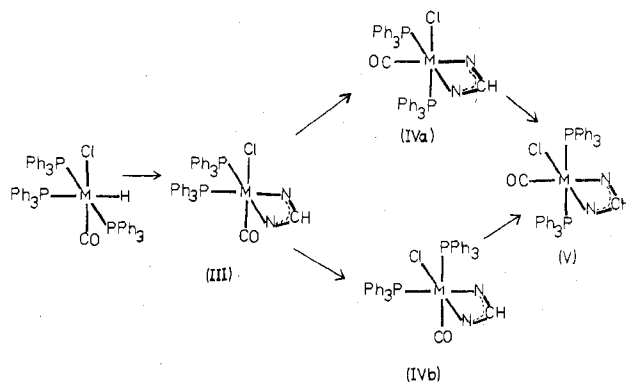
Coefficients of the Plane Equation $Ax + By + Cz = D^a$				
Plane	A	B	C	D
1	0.028	-11.753	3.712	-2.378
2	-0.129	-11.777	3.212	-2.759
3 ^b	14.730	9.254	-7.588	3.783
4 ^c	-10.939	10.037	10.543	7.859
Deviations of Various Atoms from the Planes, A				
Atom	Plane 1	Plane 2		
Ru	0.0000 (4) ^d	0.0005 (4)		
N(1)	-0.003 (5)	-0.032 (5)		
C(2)	0.006 (6)	-0.008 (6)		
N(2)	-0.003 (5)	0.007 (5)		
C(1)	-0.048	-0.021 (7)		
O(1)	-0.068	-0.023 (5)		
C(3)	0.207	0.071		
C(4)	1.219	1.311		
H(1)	-0.088	-0.10 (6)		
Dihedral Angles between Planes, Deg				
Plane 1-plane 2	1.08	Plane 2-plane 3	-37.11	
Plane 1-plane 3	-37.35	Plane 2-plane 4	-35.93	
Plane 1-plane 4	-36.31	Plane 3-plane 4	69.78	

^a The plane is in crystal coordinates. ^b Plane of rigid group PH1 (bonded to N(1)). ^c Plane of rigid group PH2 (bonded to N(2)). ^d Numbers with estimated standard deviations given in parentheses indicate the atoms which determined each of the least-squares planes.

observation was made in the triazenido structure.²⁴ Since the N-C-N angle of 114.7 (5)° is much larger than the analogous N-N-N angle of 105.2 (3)° of the triazenido structure, there is less strain in the four-membered Ru-N-C-N ring. The effect of this larger angle is also seen in the lengthening of the ruthenium-nitrogen bond lengths as compared with those in the triazenido structure. Finally, it must be emphasized that the triazenido structure, unlike the formamidinato structure reported here, is disordered²⁴ and definitive comparisons between the two are therefore limited.

As mentioned in the Introduction the structure of *trans*-RuH(dtfa)(CO)(PPh₃)₂ is the first reported in which a bidentate amidinato ligand is coordinated to a transition metal. Cotton and co-workers have reported the structures of several dimeric compounds in which a benzamidinato ligand bridges the two dimer halves.^{17,18} In addition, structural studies of seven-coordinate tantalum complexes containing bidentate amidinato ligands have been made.^{20,21} The relevant structural parameters of these structures and the formamidinato structure presented here are compared in Table XI. In most cases, the standard deviations are too large for meaningful comparison, but some observations can be made. For the tantalum compounds, the N-C-N angle is smaller with correspondingly shorter metal-nitrogen bond lengths. For the reported bridging species the N-C-N angles average 117°, an increase over the corresponding values in the bidentate structures. A similar

Scheme I



angular relationship has been found in the bridging and bidentate triazenido complexes.³³ All of the complexes given in Table XI have equivalent N-C bond distances within the N-C-N moiety.

Preparations and Spectroscopic Studies. All the complexes reported here, including the one subjected to x-ray diffraction study, display infrared bands at ca. 1540, 1510, 1280-1270, 920, and 820 cm⁻¹ which appear to be characteristic of the chelated dtfa ligand. Previous authors have reported¹⁶ the band at ca. 1540 cm⁻¹ but have not noted the much weaker bands at ca. 1280-1270, 920, and 820 cm⁻¹.

The hydrides MHX(CO)(PPh₃)₃ (M = Ru or Os; X = Cl, Br, or OCOCF₃) react with *N,N'*-di-*p*-tolylcarbodiimide to give products of stoichiometry MX(dtfa)(CO)(PPh₃)₂ (Scheme I). The ruthenium complexes RuX(dtfa)(CO)(PPh₃)₂ (X = Cl or Br) are assigned stereochemistry V on the basis of their NMR data [$\tau(\text{CH})$ ca. 2.2 t, $^4J(\text{PH})_{\text{cis}}$ = ca. 2.65 Hz; $\tau(\text{Me})$ ca. 7.78 and 7.84]. The NMR data for the corresponding trifluoroacetate, Ru(OCOCF₃)(dtfa)(CO)(PPh₃)₂, are ambiguous [$\tau(\text{CH})$ masked by aryl resonance; $\tau(\text{Me})$ 7.75 s, $\delta(\text{PPh}_3)$ 35.5 ppm (s)]; the apparent equivalence of the *p*-tolyl groups implies the presence of a symmetrically coordinated formamidinato ligand and thus favors stereochemistry III. However, as we have noted above, asymmetric coordination of the dtfa ligand is not always reflected in the NMR pattern of the *p*-tolyl groups. We therefore conclude that the trifluoroacetate complex probably possesses the same stereochemistry, V, as the chloro and bromo analogues. The corresponding osmium complexes OsX(dtfa)(CO)(PPh₃)₂, prepared under similar conditions, are assigned a different stereochemistry (IVa or b) on the basis of their NMR spectra [$\tau(\text{CH})$ ca. 0.9-1.3 d of d, $^4J(\text{PH})_{\text{trans}}$ = ca. 6 Hz, $^4J(\text{PH})_{\text{cis}}$ = ca. 2.5 Hz; $\tau(\text{Me})$ ca. 7.75 s and 7.76 s, $\delta(\text{PPh}_3)$ (X = Br) AB pattern 4.71 and -1.85 ppm, $^2J(\text{PP}')$ = 9.75 Hz]. The NMR data for the central formamidinato proton and the phosphorus nuclei establish the asymmetric situation of the dtfa ligand in these complexes. Once more, however, this asymmetry is not reflected in the NMR pattern of the *p*-tolyl

Table XI. Structural Parameters for Reported Amidinato Complexes

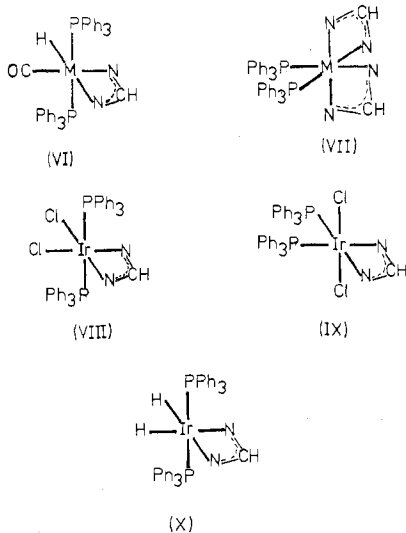
Complex ^a	M-N, A	N-C, A	N-C-N, deg	N-M-N, deg	Ref
[Mo(dpb) ₂] ₂ ^b	2.15 (1)	1.35 (1)	117 (1)		17
Re ₂ (dpb) ₂ Cl ₂ ^b	2.06 (2)	1.36 (3)	116 (2)		18
Re ₂ (dpb) ₂ Cl ₄ (THF) ^b	2.08 (1)	1.34 (2)	117 (2)		18
TaCl ₂ (dca) ₂ CH ₃ ^c	2.04 (2)	1.36 (3)	106 (2)	61.0 (7)	21
	2.19 (2)				
TaCl ₃ (dia) ₂ ^c	2.08 (2)	1.36 (3)	107 (2)	61.2 (7)	20
	2.19 (2)				
<i>trans</i> -RuH(CO)(dtfa)(PPh ₃) ₂ ^c	2.183 (6)	1.312 (7)	114.7 (5)	59.8 (2)	This work
	2.248 (5)				

^a The tabulated values have been averaged where more than one chemically equivalent parameter is present. dpb = *N,N'*-diphenylbenzamidinato, dca = *N,N'*-dicyclohexylacetamidinato, dia = *N,N'*-diisopropylacetamidinato. ^b Amidinato ligand bridges two metal centers.

^c Bidentate bonding mode.

groups. The NMR data are insufficient to distinguish between the two alternative stereochemical arrangements (IVa or b). However, the infrared data [$\nu(\text{CO})$ ca. 1940 cm^{-1}] are consistent with the presence of carbonyl trans to nitrogen rather than phosphorus and therefore favor IVa. Under more vigorous and/or prolonged reaction conditions the osmium complexes isomerize to give products of stereochemistry V, analogous to those obtained for ruthenium. It seems probable that the formation and isomerization of the ruthenium and osmium complexes $\text{MX}(\text{dtfa})(\text{CO})(\text{PPh}_3)_2$ follow a sequence (Scheme I) analogous to that proposed for the corresponding dithioformato $\text{MX}(\text{S}_2\text{CH})(\text{CO})(\text{PPh}_3)_2$ and *N*-alkyl- or *N*-aryltioformamido $\text{MX}(\text{S}^-\text{CH}^-\text{NR})(\text{CO})(\text{PPh}_3)_2$ complexes. The failure to detect the proposed intermediate isomers (III, $\text{M} = \text{Os}$; III or IV, $\text{M} = \text{Ru}$) probably reflects the vigorous and/or prolonged treatment necessary to induce reaction between carbodiimides and the precursors $\text{MHX}(\text{CO})(\text{PPh}_3)_3$ on the one hand and the relatively high lability of the coordinated formamidinato ligands on the other. Products of stereochemistry III have been observed as intermediate species in the isomerization reactions of the analogous but less labile dithioformato and thioformamidinato complexes.

The dihydrides $\text{MH}_2(\text{CO})(\text{PPh}_3)_3$ ($\text{M} = \text{Ru}$ or Os) react with *N,N'*-di-*p*-tolylcarbodiimide to yield products of stoichiometry $\text{MH}(\text{dtfa})(\text{CO})(\text{PPh}_3)_2$. The new complexes are assigned stereochemistry VI on the evidence afforded by their



NMR spectra [$\text{M} = \text{Ru}$, $\tau(\text{MH})$ 23.37 t, $^2J(\text{PH}) = 20\text{ Hz}$; $\tau(\text{CH})$ masked, $\tau(\text{Me})$ 7.75 and 7.90; $\text{M} = \text{Os}$, $\tau(\text{MH})$ 24.58 t, $^2J(\text{PH}) = 17.3\text{ Hz}$; $\tau(\text{CH})$ 1.38, $\tau(\text{Me})$ 7.75 and 7.90]. This stereochemical assignment has been confirmed by the x-ray structure of the ruthenium complex, as discussed in the previous section. Attempts to induce reaction between a second carbodiimide moiety and the remaining hydrido ligand gave only intractable products.

In contrast the dihydride $\text{RuH}_2(\text{PPh}_3)_4$ and the tetrahydride $\text{OsH}_4(\text{PPh}_3)_3$ react relatively readily with *N,N'*-di-*p*-tolylcarbodiimide to afford the complexes $\text{M}(\text{dtfa})_2(\text{PPh}_3)_2$. All attempts to isolate the intermediate species $\text{MH}(\text{dtfa})(\text{PPh}_3)_3$ were unsuccessful.

The ^1H NMR data for the complexes $\text{M}(\text{dtfa})_2(\text{PPh}_3)_2$ clearly indicate the presence of nonequivalent tolyl groups [$\tau(\text{Me})$ 7.82 and 7.90 ($\text{M} = \text{Ru}$); 7.79 and 7.84 ($\text{M} = \text{Os}$)] and thus establish stereochemistry VII, similar to that found for the corresponding dithioformato and thioformamido complexes.

The reactions of *N,N'*-di-*p*-tolylcarbodiimide with $\text{IrHCl}_2(\text{PPh}_3)_3$ (trans chlorides) and *mer*- $\text{IrH}_3(\text{PPh}_3)_3$ afford

products of stoichiometry $\text{IrCl}_2(\text{dtfa})(\text{PPh}_3)_2$ and $\text{IrH}_2(\text{dtfa})(\text{PPh}_3)_2$, respectively. The NMR data for the dichloro complex [$\tau(\text{CH})$ 0.68 t, $^4J(\text{PH})_{\text{cis}} = 1.75\text{ Hz}$, $\tau(\text{Me})$ 7.85 s], in particular the relatively small magnitude of $^4J(\text{PH})$, favor stereochemistry VIII rather than IX. The failure of the complex to isomerize on prolonged reflux in toluene is also consistent with stereochemistry VIII. The dihydrido complex $\text{IrH}_2(\text{dtfa})(\text{PPh}_3)_2$ can be unambiguously assigned stereochemistry X on the basis of NMR data [$\tau(\text{IrH})$ 32.76 t, $^2J(\text{PH})_{\text{cis}} = 17\text{ Hz}$; $\tau(\text{CH})$ 0.97 br, $\tau(\text{Me})$ 7.85 s].

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Registry No. $\text{RuCl}(\text{dtfa})(\text{CO})(\text{PPh}_3)_2$, 60939-08-4; $\text{RuBr}(\text{dtfa})(\text{CO})(\text{PPh}_3)_2$, 63915-37-7; $\text{Ru}(\text{OCOCF}_3)(\text{dtfa})(\text{CO})(\text{PPh}_3)_2$, 63915-36-6; $\text{RuH}(\text{dtfa})(\text{CO})(\text{PPh}_3)_2$, 60939-10-8; $\text{Ru}(\text{dtfa})_2(\text{PPh}_3)_2$, 60939-12-0; $\text{OsCl}(\text{dtfa})(\text{CO})(\text{PPh}_3)_2(\text{IVa})$, 63975-73-5; $\text{OsBr}(\text{dtfa})(\text{CO})(\text{PPh}_3)_2(\text{IVa})$, 63975-74-6; $\text{Os}(\text{OCOCF}_3)(\text{dtfa})(\text{CO})(\text{PPh}_3)_2(\text{IVa})$, 63915-35-5; $\text{OsCl}(\text{dtfa})(\text{CO})(\text{PPh}_3)_2(\text{V})$, 60939-09-5; $\text{OsBr}(\text{dtfa})(\text{CO})(\text{PPh}_3)_2(\text{V})$, 63915-19-5; $\text{OsH}(\text{dtfa})(\text{CO})(\text{PPh}_3)_2$, 60939-11-9; $\text{Os}(\text{dtfa})_2(\text{PPh}_3)_2$, 60939-13-1; $\text{IrCl}_2(\text{dtfa})(\text{PPh}_3)_2$, 60939-14-2; $\text{IrH}_2(\text{dtfa})(\text{PPh}_3)_2$, 60939-15-3; $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$, 16971-33-8; $\text{RuH}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2$, 63701-15-5; $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$, 25360-32-1; $\text{RuH}_2(\text{PPh}_3)_4$, 19529-00-1; $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$, 16971-31-6; $\text{OsH}(\text{OCOCF}_3)(\text{CO})(\text{PPh}_3)_2$, 63701-16-6; $\text{OsH}(\text{CO})(\text{PPh}_3)_3$, 63915-27-5; $\text{OsH}_4(\text{PPh}_3)_3$, 24228-59-9; *trans*- $\text{IrCl}_2\text{H}(\text{PPh}_3)_3$, 28060-70-0; *mer*- $\text{IrH}_3(\text{PPh}_3)_3$, 18660-47-4; *N,N'*-di-*p*-tolylcarbodiimide, 726-42-1.

Supplementary Material Available: Table I, analytical and melting point data, Table VII, the root-mean-square amplitudes of vibration, Table VIII, the idealized positions of the hydrogen atoms, and a listing of the observed and calculated structure amplitudes (42 pages). Ordering information is given on any current masthead page.

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Contribution from the Faculty of Science,
 University of Regina, Regina, Saskatchewan, Canada S4S 0A2

Coordination Polyhedra with Nine and Ten Atoms¹

B. E. ROBERTSON

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An irregular nine-coordinate polyhedron may be characterized by comparing it to two polytopal nine-coordinate polyhedra, the D_{3h} tricapped trigonal prism and the C_{4v} monocapped square antiprism. An irregular ten-coordinate polyhedron may be characterized by comparing it to two polytopal ten-coordinate polyhedra, the D_{4d} bicapped square antiprism and a C_{2v} decatetrahedron which is closely related to the Hoard dodecahedron. A sensitive indication of polyhedral type is provided by the set of dihedral angles formed by the two faces meeting at each edge of the polyhedron (the δ parameters introduced by Porai-Koshits and Aslanov). The set of δ angles for the aforementioned polytopes have been calculated and they show that the transition from the tricapped trigonal prism to the monocapped square antiprism is characterized by a change in the δ at one edge of the former from ca. 26.4 to 0° in the latter. The transition from the bicapped square antiprism to the decatetrahedron is characterized by a change in the δ at two edges in the former from ca. 30.9 to 0° in the latter.

Introduction

To a first order of approximation, the average quantity of discussion of a coordination polyhedron appears to be inversely proportional to the number of atoms in the coordination sphere. There exist several plausible explanations for this phenomenon, some of which follow.

Polyhedra with higher coordination number often contain chelating ligands which are themselves asymmetric and which pack to form low-symmetry space groups. The point groups of some large symmetric coordination polyhedra, such as the icosahedron and derivatives thereof, are not consistent with the demands of translational symmetry, and therefore must become distorted in order to be tessellated. Therefore, in the solid state, such polyhedra often show either low point symmetry or none at all.

In the event that the coordination polyhedron does not approximate to one with a nontrivial point symmetry operation, it is generally assumed that there is little to be gained from detailed consideration of its geometry. Coordination polyhedra of larger coordination number are often identified by investigators solely by inspection. It would therefore seem relevant to add the somewhat trivial remark that such polyhedra are not easily visualized.

Those authors of crystallographic reports who consider the distortions of a polyhedron from the appropriate reference polyhedra (polytopes) have used several related approaches. Day and Hoard² discussed the distorted monocapped square antiprismatic coordination polyhedron in $\text{ThT}_4(\text{CH}_3)_2\text{NCHO}$ (where T is the tropolonato ligand $\text{C}_7\text{H}_5\text{O}_2$) in terms of the less symmetric stereoisomers allowed by the bidentate tropolonato ligands. Many authors have adopted a criterion first suggested by Porai-Koshits and Aslanov³ which allows for a quantitative assessment of polyhedral type. This criterion makes use of the set of dihedral angles, δ , formed by the pairs

of faces that meet at each edge of the polyhedron. Porai-Koshits and Aslanov, in their original discussion, presented reference data only for eight-coordinate polyhedra. Muetterties and Guggenberger⁴ have extended the analysis to lower coordination polyhedra. At that time they also indicated their intention to pursue the analysis of nine-coordinate polyhedra. We recently found ourselves in need for some basis for the discussion of a nine-coordinate polyhedron and therefore undertook the analysis of both nine- and ten-coordinate polyhedra. Since then the results of Guggenberger and Muetterties have appeared in print.⁵ However, the approach we have taken here is a somewhat different one than that of the latter authors.

Identification of Polyhedra

The most straightforward basis for the comparison or identification of polyhedra is the number of faces meeting at each vertex (the order of the vertices) and the positions of the vertices of given order in the polyhedron with respect to each other. In practice, this technique has at least two shortcomings if no other parameters are considered: (i) it does not give any estimation of the degree of distortion from the idealized polyhedron which is approximated, and (ii) in order to properly count the faces meeting at a vertex it is first necessary to decide if four or more vertices are sufficiently near to the least-squares plane through them that they should be considered as forming a nontriangular face. It is not possible to give an a priori lower limit for these out-of-plane distances which will be universally applicable.

In order to obtain further information as to the best description of a polyhedron and, in addition, information concerning the nature of the distortions from ideal geometry, one may also consider the relative lengths of the edges of the polyhedron and the angles subtended at the central cation. However, edge lengths tend to be insensitive to changes in