

one coordinated anion, and the metal ion is five-coordinate, with a CuN_4O core. Upon increasing the size of the coordinated anion, from nitrate to trifluoromethanesulfonate, a progressive structural distortion of the complex from nearly square pyramidal to nearly trigonal bipyramidal results. The trifluoromethanesulfonate anion must be considered a weak ligand, and its coordinating ability appears to be intermediate between that of the perchlorate and nitrate anions. In solution these Cu(II) complexes appear more regular because the bulky trifluoromethanesulfonate ions are displaced by solvent molecules. The EPR spectra from frozen solutions are typical for nearly tetragonal symmetry, in accordance with the finding that in solution the symmetry of the ligand field is higher than the ligand geometry.⁴³ The optical spectra, though in general not especially good indicators of geometry for copper(II) complexes, seem more sensitive to small differences in the coordination environment. Appreciable distortions from tet-

ragonal geometry, comparable with those occurring in the solid state, are evidenced by the EPR spectra from frozen solutions when chloride or bromide ions coordinate to the copper(II)-tapp and -tipp complexes. Rather drastic changes, in these cases, are also observed in the optical spectra.

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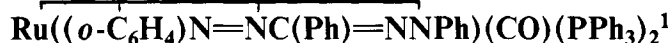
Registry No. tipp, 77136-33-5; tapp, 77136-34-6; tid, 77136-35-7; $[\text{Cu(tipp)}][\text{ClO}_4]$, 77136-46-0; $[\text{Cu(tapp)}][\text{ClO}_4]$, 77152-65-9; $[\text{Cu(tid)}][\text{ClO}_4]$, 77136-48-2; $[\text{Cu(tipp)}][\text{ClO}_4]_2$, 77136-50-6; $[\text{Cu(tapp)}][\text{ClO}_4]_2$, 77136-52-8; $[\text{Cu(tipp)}(\text{OSO}_2\text{CF}_3)][\text{OSO}_2\text{CF}_3]$, 77136-54-0; $[\text{Cu(tipp)}(\text{ONO}_2)][\text{NO}_3]$, 77136-56-2; $[\text{Cu(tapp)}(\text{ONO}_2)][\text{NO}_3]$, 77136-58-4; $[\text{Cu(tapp)}(\text{OSO}_2\text{CF}_3)][\text{OSO}_2\text{CF}_3]$, 77152-67-1; $[\text{Cu}(\text{MeCN})_4][\text{ClO}_4]$, 14057-91-1; 2-thiophenecarboxaldehyde, 98-03-3; N,N' -bis(3-aminopropyl)piperazine, 7209-38-3; 1,10-decanediamine, 646-25-3.

Supplementary Material Available: A listing of structure amplitudes (Table III) (8 pages). Ordering information is given on any current masthead page.

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Cyclometalated Formazan Derivatives of Ruthenium and Osmium: Structure of



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1,5-Diphenylformazans, $\text{PhN}=\text{NC}(\text{R})=\text{NNHPh}$ ($\text{R} = \text{H, Me, or Ph}$), react with the complexes $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$, $\text{RuH}_2(\text{CO})(\text{AsPh}_3)_3$, $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$, $\text{Os}(\text{O}_2\text{CCF}_3)_2(\text{CO})(\text{PPh}_3)_2$, and $\text{OsH}(\text{O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2$ in boiling 2-methoxyethanol or dimethylformamide over a period of 30 min to 4 h to afford cyclometalated formazan derivatives $\text{M}((o\text{-C}_6\text{H}_4)\text{N}=\text{NC}(\text{R})=\text{NNPh})(\text{CO})(\text{EPh}_3)_2$ ($\text{M} = \text{Ru, E} = \text{P, R} = \text{H, Me, or Ph}$; $\text{M} = \text{Ru, E} = \text{As, R} = \text{Ph}$; $\text{M} = \text{Os, E} = \text{P, R} = \text{H, Me, or Ph}$) as deep green, air-stable, crystalline solids. The initial products formed in these reactions appear to be N^1, N^5 -chelate formazan complexes which subsequently rearrange and undergo cyclometalation. Isomeric intermediates of the form $\text{Ru}(\text{PhN}=\text{NCH}=\text{NNPh})\text{H}(\text{CO})(\text{PPh}_3)_2$ have been isolated as pink (*cis*- PPh_3 ligands) or purple (*trans*- PPh_3 ligands) complexes from the reaction of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ with $\text{PhN}=\text{NCH}=\text{NNHPh}$ and have been shown to convert to the green cyclometalated complex $\text{Ru}((o\text{-C}_6\text{H}_4)\text{N}=\text{NCH}=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$ on further heating. The structure of the green complex $\text{Ru}((o\text{-C}_6\text{H}_4)\text{N}=\text{NC}(\text{Ph})=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$ has been established by an X-ray diffraction study. The complex crystallizes in space group $\text{C}_{2h}^2\text{-P2}_1/\text{c}$ ($a = 18.539$ (3) Å, $b = 25.381$ (6) Å, $c = 19.391$ (4) Å, $\beta = 97.36$ (1)° at 0 °C) with two pseudosymmetrically related molecules per asymmetric unit. The structure, described by 399 variable parameters, was refined with use of 8498 reflections having $F_o^2 > 3\sigma(F_o^2)$ to values for R and R_w of 0.081 and 0.107. The compound contains six-coordinated ruthenium(II) bound to a trans pair of triphenylphosphine ligands (average $\text{Ru-P} = 2.384$ (5) Å), a carbonyl group (average $\text{Ru-C} = 1.83$ (1) Å, $\text{C-O} = 1.17$ (1) Å), and a planar, tridentate, cyclometalated formazan ligand coordinated through nitrogen atoms N^1 ($\text{Ru-N} = 2.163$ (7) Å) and N^4 ($\text{Ru-N} = 2.02$ (1) Å) and the ortho carbon atom of the phenyl ring on the N^5 nitrogen atom ($\text{Ru-C} = 2.091$ (9) Å). The bond lengths found for the formazan skeleton are consistent with extensive electron delocalization throughout the chelate rings and the adjoining phenyl groups.

Introduction

Formazan, $\text{NH}^1=\text{N}^2\text{CH}^3=\text{N}^4\text{N}^5\text{H}_2$, is the hypothetical parent member of a series of 1,5- or 1,3,5-substituted formazans ($\text{ArN}=\text{NCR}=\text{NNHAr}$, where $\text{Ar} = \text{aryl}$ and $\text{R} = \text{H, alkyl, or aryl}$), the first examples of which were synthesized in 1892 by Bamberger³ and von Pechmann.⁴ Subsequent

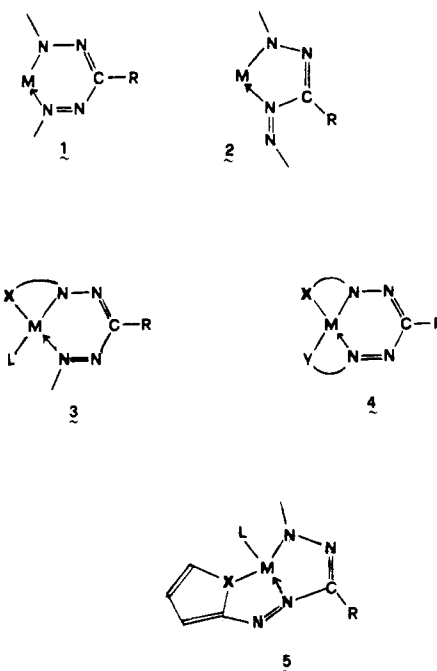
workers have introduced a wide variety of functional groups onto the 1-, 3-, and 5-substituents to generate a diverse range of formazans,^{5,6} which have found important applications as colorimetric agents,⁷ metal extractants,⁸ pigments,⁹⁻¹¹ and

- (1) This is part 21 of Complexes of the Platinum Metals. For part 20, see: Harris, A. D.; Robinson, S. D.; Sahajpal, A.; Hursthouse, M. B., submitted for publication in *J. Chem. Soc., Dalton Trans.*
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biological redox indicators.^{12,13} Introduction of functional substituents on the 3-position of 1,5-diphenylformazan affords important analytical reagents, including dithizone (3-SH)¹⁴ and zincon (3-OH).¹⁵ However, the obvious potential of formazan derivatives as ligands for transition metals has attracted remarkably little attention. Stability constants¹⁶ and/or kinetic data¹⁷ have been measured for formazan complexes of many transition and nontransition metals, particularly those displaying class "b" character. However, relatively few products of this type have been isolated and fully characterized. Most known transition-metal formazan complexes involve first-row ions, particularly cobalt(II), nickel(II), and copper(II)¹⁸⁻²¹ or copper(I).^{19,22} Few examples containing second- or third-row transition metals have been established. To the best of our knowledge only the series of rhodium formazan complexes $\text{Rh}(\text{ArN}=\text{NC}(\text{R})=\text{NNAr})(\text{CO})_2$ ($\text{R} = \text{Me}$ or Ph , $\text{Ar} = \text{aryl}$ or heteroaryl)²³ and, very recently, bis(1,3,5-triarylformazanyl)palladium and (1,3,5-triarylformazanyl)palladium hexafluoroacetylacetonate²⁴ have previously been characterized.

X-ray diffraction^{24,25} and spectroscopic studies^{26,27} have established that in the bis chelate complexes of 1,5-diaryl- or 1,3,5-triarylformazans with cobalt(II),^{26,27} nickel(II),²⁵⁻²⁷ copper(II),²⁶⁻²⁸ and palladium(II)²⁴ ions coordination occurs through the terminal nitrogen atoms, N^1 and N^5 , of the formazan skeleton (1). Bonding through nitrogen atoms N^1 and N^4 to generate a five-membered chelate ring (2) has been considered for some nickel(II) formazan derivatives but dismissed as improbable.²⁹ Functionally substituted formazans containing potential donor sites on one or both of the N^1 and N^5 substituents frequently serve as tridentate (3) or tetradentate (4) ligands, respectively.^{5,11} N^1, N^4 -Coordination of the formazan skeleton (5)—to accommodate the steric requirements of the third and/or fourth donor sites—has been considered for a number of products of this type,^{30,31} but



structures based on N^1, N^5 -coordination of the formazan group are generally preferred. In the present paper we report formation of the first aryl formazan complexes of ruthenium and osmium and describe their facile conversion to a series of stable products containing the first examples of tridentate cyclometalated formazan ligands. The latter products also appear to be the first fully established examples of complexes containing N^1, N^4 -chelated formazan ligands.

The synthesis, organic reactions, applications, and coordination chemistry of simple and/or functionally substituted formazans have been extensively reviewed elsewhere.^{5,6,31,32}

Experimental Section

Ruthenium and osmium salts were supplied by Johnson Matthey and Co. Ltd. Ruthenium and osmium phosphine complexes^{33,34} and aryl formazans³² were prepared by standard literature procedures. All reactions were performed under a nitrogen atmosphere, but the products were worked up in the presence of air. Analyses were performed at the Analytical Laboratory, University College, London. Melting points were taken in sealed tubes under nitrogen. Proton and ³¹P NMR spectra were obtained in CDCl_3 solution at 90 and 36.44 MHz, respectively, with use of a Bruker HFX90 spectrometer operating in Fourier transform mode and are referenced to internal Me_4Si and external H_3PO_4 , respectively. Positive values for ³¹P chemical shifts correspond to resonances at low field relative to H_3PO_4 . Infrared spectra were taken on a Perkin-Elmer 457 grating spectrometer using samples mullied in Nujol.

Preparation of $\text{Ru}((o\text{-C}_6\text{H}_4)\text{N}=\text{NC}(\text{Ph})=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$.
A. From $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$. Carbonylchlorohydridotris(triphenylphosphine)ruthenium (0.3 g, 0.31 mmol) and 1,3,5-triphenylformazan (0.12 g, 0.4 mmol) were heated together under reflux in 2-methoxyethanol (4 mL) for 4 h. The solution was cooled to ambient temperature, filtered, diluted with methanol (25 mL), and then set aside to crystallize. The precipitate which slowly formed was filtered off after 5 days, washed successively with methanol (10 mL) and hexane (10 mL), and then dried in vacuo to yield the required product (0.14 g, 47%) as fine dark green crystals (mp 248 °C with

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dec, $\nu(\text{CO}) = 1920 \text{ cm}^{-1}$, $\delta(\text{P}) 34.07$). Anal. Calcd for $\text{C}_{56}\text{H}_{44}\text{N}_4\text{O}_2\text{P}_2\text{Ru}$: C, 70.65; H, 4.66; N, 5.89. Found: C, 70.35; H, 4.35; N, 5.7.

B. From $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$. Carbonyldihydridotris(triphenylphosphine)ruthenium (0.2 g, 0.22 mmol) and 1,3,5-triphenylformazan (0.12 g, 0.4 mmol) were heated together under reflux in 2-methoxyethanol (4 mL) for 30 min. The resultant solution was worked up as described above to afford the required product (0.17 g, 82%) which was identical with an authentic sample. Anal. Found: C, 70.41; H, 4.58; N, 5.78.

Preparation of $\text{Ru}((o\text{-C}_6\text{H}_4)\text{N}=\text{NC}(\text{Me})=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$ from $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$. The title compound was prepared from carbonyldihydridotris(triphenylphosphine)ruthenium and 3-methyl-1,5-diphenylformazan in 2-methoxyethanol by the method described above and was isolated in 59% yield as fine dark green crystals (mp 247–248 °C with dec, $\nu(\text{CO}) = 1915 \text{ cm}^{-1}$, $\delta(\text{P}) 34.68$). Anal. Calcd for $\text{C}_{51}\text{H}_{42}\text{N}_4\text{O}_2\text{P}_2\text{Ru}$: C, 68.83; H, 4.76; N, 6.30. Found: C, 68.84; H, 4.80; N, 6.38.

Preparation of $\text{Ru}((o\text{-C}_6\text{H}_4)\text{N}=\text{NCH}=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$ from $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$. The title compound was prepared from carbonyldihydridotris(triphenylphosphine)ruthenium and 1,5-diphenylformazan in 2-methoxyethanol by the method described above, except that a reflux time of 1 h was employed, and was isolated in 55% yield as fine dark green crystals (mp 261–263 °C with dec, $\nu(\text{CO}) = 1920$ (s) and 1910 (vs) cm^{-1} , $\delta(\text{P}) 34.40$). Anal. Calcd for $\text{C}_{50}\text{H}_{40}\text{N}_4\text{O}_2\text{P}_2\text{Ru}$: C, 68.56; H, 4.60; N, 6.40. Found: C, 68.32; H, 4.77; N, 6.01.

Preparation of $\text{Ru}(\text{PhN}=\text{NCH}=\text{NNPh})\text{H}(\text{CO})(\text{PPh}_3)_2$ (Two Isomers). Carbonyldihydridotris(triphenylphosphine)ruthenium (0.2 g, 0.22 mmol) and 1,5-diphenylformazan (0.11 g, 0.5 mmol) were heated together under reflux in 2-methoxyethanol (4 mL) for 20 min. The solution was cooled to ambient temperature, filtered, diluted with methanol (25 mL), and set aside to crystallize. The dark purple crystals (0.11 g) which separated were filtered off, washed successively with methanol (10 mL) and hexane (10 mL), and then dried in vacuo. A sample of this product was chromatographed on a silica gel column (10 × 2.5 cm). Elution with dichloromethane removed a pink band followed by a green band and left behind a purple band which was subsequently eluted with a 2:1 mixture of ethanol and dichloromethane. On standing in dichloromethane solution the pink material spontaneously converted to the purple product. Evaporation of the eluate fractions gave pink (ca. 5%), purple (ca. 55%), and green (ca. 40%) solid products. The pink compound ($\nu(\text{CO}) = 1973$ and 1960 cm^{-1} , $\delta(\text{P}) 22.43$) was not isolated in sufficient quantity to permit satisfactory elemental analysis but was identified by spectroscopic techniques as

$\text{Ru}(\text{PhN}=\text{NCH}=\text{NNPh})\text{H}(\text{CO})(\text{PPh}_3)_2$ (*cis*- PPh_3 ligands). The purple compound (mp 152–156 °C with dec, $\nu(\text{CO}) = 1935 \text{ cm}^{-1}$, $\delta(\text{P}) 42.19$, $\tau(\text{RuH}) = 19.7$, $^2J(\text{PH})_{\text{cis}} = 20 \text{ Hz}$) was identified by spectroscopic methods as $\text{Ru}(\text{PhN}=\text{NCH}=\text{NNPh})\text{H}(\text{CO})(\text{PPh}_3)_2$ (*trans*- PPh_3 ligands) and gave analytical results consistent with that formulation. Anal. Calcd for $\text{C}_{50}\text{H}_{42}\text{N}_4\text{O}_2\text{P}_2\text{Ru}$: C, 68.40; H, 4.82; N, 6.38. Found: C, 67.81; H, 4.92; N, 6.21. The green product was identified as $\text{Ru}((o\text{-C}_6\text{H}_4)\text{N}=\text{NCH}=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$ by comparison with an authentic sample.

Conversion of $\text{Ru}(\text{PhN}=\text{NCH}=\text{NNPh})\text{H}(\text{CO})(\text{PPh}_3)_2$ to $\text{Ru}((o\text{-C}_6\text{H}_4)\text{N}=\text{NCH}=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$. Dark purple crystals of carbonyldihydrido(1,5-diphenylformazan)bis(triphenylphosphine)ruthenium (0.05 g) were heated under reflux in 2-methoxyethanol (4 mL). After 30 min the resultant green solution was allowed to cool, then diluted with methanol (25 mL), and left to crystallize. The green crystals which deposited over a period of 12 h were filtered off, washed successively with methanol (10 mL) and hexane (10 mL), dried in vacuo, and identified as the required product by comparison with an authentic specimen.

Preparation of $\text{Ru}(o\text{-C}_6\text{H}_4)\text{N}=\text{NC}(\text{Ph})=\text{NNPh})(\text{CO})(\text{AsPh}_3)_2$ from $\text{RuH}_2(\text{CO})(\text{AsPh}_3)_3$. Carbonyldihydridotris(triphenylarsine)ruthenium (0.11 g, 0.1 mmol) and 1,3,5-triphenylformazan (0.06 g, 0.2 mmol) were heated together under reflux in 2-methoxyethanol (4 mL) for 30 min. The solution was cooled to ambient temperature, filtered, diluted with methanol (20 mL), and set aside to crystallize. After 12 h the green precipitate was filtered off, washed successively with methanol (10 mL) and hexane (10 mL), and then dried in vacuo

Table I. Data Collection Parameters for

$\text{Ru}((o\text{-C}_6\text{H}_4)\text{N}=\text{NC}(\text{Ph})=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$	
formula	$\text{C}_{56}\text{H}_{44}\text{N}_4\text{O}_2\text{P}_2\text{Ru}$
fw	952.02
space group	$\text{C}_{2h}^2\text{-P2}_1/\text{c}$
<i>a</i> , Å	18.539 (3)
<i>b</i> , Å	25.387 (4)
<i>c</i> , Å	19.391 (4)
β , deg	97.36 (1)
<i>Z</i>	8
ρ_c , g cm ⁻³	1.397
temp, °C	0
radiation	graphite-monochromated Mo K α ($\lambda(\text{Mo K}\alpha_1) = 0.7093 \text{ Å}$)
linear abs coeff, cm ⁻¹	4.52
cryst vol, mm ³	0.066 ^b
data collected	$\pm h, k, l \leq 44.3^\circ$ in 2θ
bkgd counts, s	10 at each end with rescan option ^c
scan range, deg	0.95 below K α_1 to 0.70 above K α_2
no. of unique data collected	11 411
no. of data with $F_o^2 > 3\sigma(F_o^2)$	8498
<i>R</i>	0.04

^a The low-temperature device is based upon a design by J. C. Huffman, Ph.D. Thesis, Indiana University, 1974. ^b Maximum error induced in F_o^2 by neglect of absorption is ~3%. ^c Lenhert, P. G. *J. Appl. Crystallogr.* 1975, 8, 568.

to yield the required product as fine green crystals (0.026 g (24%), mp 213–218 °C with dec, $\nu(\text{CO}) = 1915 \text{ cm}^{-1}$). Anal. Calcd for $\text{C}_{56}\text{H}_{44}\text{As}_2\text{N}_4\text{O}_2\text{Ru}$: C, 64.68; H, 4.27; N, 5.39. Found: C, 62.44; H, 4.15; N, 5.48.

Preparation of $\text{Os}((o\text{-C}_6\text{H}_4)\text{N}=\text{NC}(\text{Ph})\text{NNPh})(\text{CO})(\text{PPh}_3)_2$ from $\text{OsH}(\text{O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2$. Hydrido(trifluoroacetato)-carbonylbis(triphenylphosphine)osmium (0.15 g, 0.18 mmol) and 1,3,5-triphenylformazan (0.06 g, 0.2 mmol) were heated together under reflux in 2-methoxyethanol (4 mL) for 2 h. The solution was then cooled to ambient temperature, filtered, diluted with methanol (25 mL), and set aside to crystallize. The precipitate which slowly formed was filtered off after 5 days, washed successively with methanol (10 mL) and hexane (10 mL), and then dried in vacuo to afford the required product (0.022 g, 12%) as green crystals (mp 262 °C, $\nu(\text{CO}) = 1905 \text{ cm}^{-1}$). Anal. Calcd for $\text{C}_{56}\text{H}_{44}\text{N}_4\text{O}_2\text{OsP}_2$: C, 64.60%; H, 4.26; N, 5.38. Found: C, 63.39; H, 4.37; N, 5.32.

Use of dimethylformamide (4 mL) as solvent in place of 2-methoxyethanol gave a marginally improved yield (0.035 g, 19%).

Preparation of $\text{Os}((o\text{-C}_6\text{H}_4)\text{N}=\text{NC}(\text{Me})=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$. The title compound was prepared from hydrido(trifluoroacetato)-carbonylbis(triphenylphosphine)osmium (0.1 g, 0.12 mmol) and 3-methyl-1,5-diphenylformazan (0.15 g, 0.4 mmol) in dimethylformamide (4 mL) with the method described above and was isolated in 23% yield as dark green crystals (mp 261 °C with dec, $\nu(\text{CO}) = 1890 \text{ cm}^{-1}$). Anal. Calcd for $\text{C}_{51}\text{N}_4\text{OsP}_2$: C, 62.56; H, 4.32; N, 5.72. Found: C, 62.39; H, 4.47; N, 5.84.

Preparation of $\text{Os}((o\text{-C}_6\text{H}_4)\text{N}=\text{NCH}=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$. The title compound was similarly prepared with use of 1,5-diphenylformazan and was isolated in 20% yield as dark green crystals (mp 246–250 °C with dec, $\nu(\text{CO}) = 1890 \text{ cm}^{-1}$, $\delta(\text{P}) 5.37$). Anal. Calcd for $\text{C}_{50}\text{H}_{40}\text{N}_4\text{O}_2\text{OsP}_2$: C, 62.23; H, 4.15; N, 5.81. Found: C, 63.28; H, 4.70; N, 5.60.

Crystallographic Study of $\text{Ru}((o\text{-C}_6\text{H}_4)\text{N}=\text{NC}(\text{Ph})=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$. Symmetry and systematic absences uniquely consistent with the monoclinic space group $\text{C}_{2h}^2\text{-P2}_1/\text{c}$ were observed by precession photography. However, the pattern showed very marked pseudo B centering; that is, reflections of the type hkl , $h + l$ odd, were systematically weak. A rather ill-shaped platelike crystal was cleaved from a much larger crystal. Midway through data collection at –160 °C upon a Picker FACS-I diffractometer a small number of additional unwanted reflections corresponding to a doubling of the *c* axis were detected. A reversible phase transition was found to occur at –30 °C. Since the assumed unit cell was sufficiently large that overlap of reflections was a potential problem, data collection was begun again at 0 °C. Unit cell parameters and crystal orientation at this temperature were determined by least-squares refinements of the orien-

Table II. Positional and Thermal Parameters for the Nongroup Atoms

ATOM	X ^A	Y	Z	B ₁₁ ^B	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Ru	0.222652 (37)	0.117105 (27)	-0.505922 (36)	166.8 (27)	87.1 (14)	194.4 (25)	7.7 (14)	59.2 (19)	7.8 (14)
Ru#	-0.273720 (37)	0.122565 (27)	0.001769 (37)	152.5 (26)	80.1 (14)	233.0 (27)	5.8 (14)	65.3 (19)	4.7 (14)
P (1)	0.31904 (13)	0.096607 (95)	-0.41682 (12)	204.8 (85)	115.1 (46)	198.4 (78)	25.9 (49)	43.3 (64)	-1.0 (47)
P (2)	0.13105 (13)	0.13747 (10)	-0.60046 (13)	196.2 (87)	115.3 (45)	247.7 (84)	2.3 (50)	25.0 (67)	26.9 (49)
P (1)#	-0.17051 (13)	0.108491 (96)	0.08660 (14)	166.8 (82)	99.8 (44)	331.2 (95)	-5.0 (48)	34.7 (69)	23.1 (52)
P (2)#	-0.37379 (13)	0.138171 (96)	-0.08570 (13)	178.0 (83)	106.9 (43)	228.6 (79)	12.9 (48)	68.3 (64)	3.8 (47)

ATOM	X	Y	Z	B ₁₁ ²	ATOM	X	Y	Z	B ₁₁ ²
C (56)#	-0.28775 (50)	0.05167 (38)	-0.00701 (47)	3.42 (19)	C (56)	0.20372 (49)	0.04606 (36)	-0.51336 (45)	2.88 (18)
O (1)#	-0.29691 (39)	0.00574 (29)	-0.01324 (36)	5.08 (16)	O (1)	0.19237 (39)	0.00096 (29)	-0.51589 (36)	5.10 (16)
N (11)#	-0.33964 (38)	0.14744 (28)	0.08003 (35)	2.77 (14)	N (1)	0.15522 (37)	0.14606 (28)	-0.43094 (35)	2.79 (14)
N (3)#	-0.25399 (37)	0.20089 (27)	0.01407 (35)	2.61 (14)	N (3)	0.24951 (37)	0.19363 (27)	-0.49373 (34)	2.58 (14)
C (11)#	-0.20442 (47)	0.13825 (35)	-0.07244 (45)	3.05 (18)	C (1)	0.30007 (47)	0.12763 (34)	-0.57440 (44)	2.85 (18)
C (2)#	-0.17022 (50)	0.10763 (36)	-0.11991 (47)	3.31 (19)	C (2)	0.32628 (49)	0.09688 (35)	-0.62583 (46)	3.11 (19)
C (3)#	-0.12554 (56)	0.13020 (40)	-0.16363 (53)	4.32 (22)	C (3)	0.37794 (55)	0.11619 (40)	-0.66510 (52)	3.94 (21)
C (4)#	-0.11155 (55)	0.18290 (40)	-0.16142 (52)	4.35 (22)	C (4)	0.40388 (59)	0.16654 (44)	-0.65738 (56)	4.66 (24)
C (5)#	-0.14086 (56)	0.21464 (40)	-0.11489 (52)	4.27 (22)	C (5)	0.37922 (56)	0.19926 (41)	-0.60835 (52)	4.24 (22)
C (6)#	-0.18603 (47)	0.19219 (34)	-0.07087 (44)	2.83 (18)	C (6)	0.32669 (50)	0.18015 (36)	-0.56967 (47)	3.10 (19)
N (4)#	-0.21277 (39)	0.22671 (28)	-0.02318 (37)	3.05 (15)	N (4)	0.30029 (39)	0.21624 (28)	-0.52397 (36)	3.07 (15)
C (7)#	-0.28639 (46)	0.22648 (34)	0.06377 (43)	2.67 (17)	C (7)	0.21543 (48)	0.22213 (35)	-0.44629 (45)	2.85 (18)
C (8)#	-0.27548 (51)	0.28190 (37)	0.08382 (49)	3.43 (20)	C (8)	0.22676 (50)	0.27832 (36)	-0.43207 (47)	3.26 (19)
C (9)#	-0.27472 (64)	0.29548 (48)	0.15376 (61)	5.84 (27)	C (9)	0.22551 (54)	0.31549 (41)	-0.48406 (52)	4.01 (22)
C (10)#	-0.26573 (78)	0.34969 (60)	0.17372 (75)	7.71 (36)	C (10)	0.22997 (61)	0.36833 (45)	-0.46939 (59)	4.99 (25)
C (11)#	-0.26015 (76)	0.38644 (55)	0.12612 (75)	7.26 (34)	C (11)	0.24054 (69)	0.38597 (50)	-0.40403 (67)	6.31 (30)
C (12)#	-0.26064 (67)	0.37410 (48)	0.05793 (64)	6.06 (29)	C (12)	0.24268 (76)	0.35059 (58)	-0.35000 (73)	7.66 (35)
C (13)#	-0.26834 (56)	0.32191 (42)	0.03689 (53)	4.53 (23)	C (13)	0.23624 (64)	0.29611 (48)	-0.36338 (61)	5.70 (27)
N (2)#	-0.33166 (39)	0.19719 (28)	0.09774 (36)	3.06 (15)	N (2)	0.16748 (39)	0.19554 (28)	-0.41467 (36)	2.95 (15)
C (14)#	-0.39185 (46)	0.12129 (33)	0.11430 (43)	2.59 (17)	C (14)	0.09919 (49)	0.12411 (34)	-0.39666 (46)	2.89 (18)
C (15)#	-0.39448 (66)	0.06819 (48)	0.11515 (61)	5.70 (28)	C (15)	0.07112 (54)	0.14897 (39)	-0.34421 (51)	3.97 (21)
C (16)#	-0.44566 (71)	0.04087 (49)	0.14890 (65)	6.37 (30)	C (16)	0.01393 (62)	0.12667 (44)	-0.31421 (57)	5.12 (25)
C (17)#	-0.49656 (60)	0.06719 (44)	0.17808 (56)	4.68 (24)	C (17)	-0.01662 (62)	0.08086 (46)	-0.33913 (59)	5.32 (26)
C (18)#	-0.49713 (70)	0.11989 (50)	0.17470 (64)	5.93 (30)	C (18)	0.01043 (63)	0.05485 (44)	-0.39177 (59)	5.46 (26)
C (19)#	-0.44474 (59)	0.14702 (43)	0.14365 (55)	4.96 (24)	C (19)	0.06949 (55)	0.07641 (39)	-0.42056 (51)	4.01 (21)

^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 ellipsoid 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 $\times 10^5$.

tation angles of 37 centered reflections³⁵ in the range $36.5^\circ < 2\theta(\text{Mo K}\alpha_1) < 37.5^\circ$. Other data collection parameters are summarized in Table I.

Standard procedures and programs were used to solve and refine this structure.³⁵ Initial calculations were done with use of the Northwestern University CDC 6600 computer. Final calculations were performed on the Lawrence Berkeley Laboratory CDC 7600 system.

The pseudosymmetry of the diffraction pattern was preserved in the Patterson map where it was clear that pairs of Ru and P atoms were pseudosymmetrically related by $x + 1/2, y, z + 1/2$. Fortunately, MULTAN78, with scaling such that each parity group had the same average E value, produced a solution to this problem of 128 atoms per asymmetric unit. The Ru and P atoms and most of the two triphenylformazan fragments were apparent. Subsequent Fourier syntheses interspersed with cycles of full-matrix least-squares refinements revealed the remainder of the structure, including some of the phenyl hydrogen atoms in the penultimate difference Fourier map. These were included at their calculated idealized geometry (C-H = 0.95 Å, C-C-H = 120°). Full-matrix least-squares refinement converged at values for R and R_w of 0.081 and 0.107, respectively, for a model comprising six atoms (Ru and P) refined with anisotropic thermal parameters, 50 atoms and 12 rigid phenyl groups refined with isotropic thermal parameters, a total of 399 variable parameters.

Large thermal motion and/or orientational disorder appears to occur in two of the phosphine phenyl groups, as indicated by the high thermal parameters for some atoms. Refinements in which reflections of the type $hkl, h + l$ odd, were given greater weight produced no significant improvement. There is no significant correlation between parameters of independent molecules 1 and 2, and at all times the geometry of the triphenylformazan moiety remained unaffected by the model employed for phenyl scattering. With little prospect of improved

metrical details in the chemically interesting part of the structure, the enormous expense involved in releasing group restraints and allowing full anisotropic refinement was judged to be unwarranted.

The final difference Fourier map was mostly flat and featureless with residual electron density (highest peak 1.3 e Å⁻³) being concentrated around two phosphine phenyl groups. The value of the minimized function was independent of the magnitude of ranges of $|F_o|$ and exhibited only a slight dependence on the ranges of $\lambda^{-1} \sin \theta$, indicating that the weighting scheme was satisfactory. Final parameters for nonhydrogen atoms are given in Table II; rigid group parameters are given in Table III. Table IV³⁶ lists hydrogen atom parameters, and a listing of $10|F_o|$ vs. $10|F_c|$ is available.³⁶

Results and Discussion

Synthesis. The complexes RuHCl(CO)(PPh₃)₃ and RuH₂(CO)(PPh₃)₃ react with 1,5-diphenylformazans, PhN=NC(R)=NNHPh (R = H, Me, or Ph), in boiling 2-methoxyethanol to evolve dihydrogen and afford stable, green crystalline products containing one carbonyl, two triphenylphosphine ligands, and one formazan-based group per ruthenium atom. The corresponding osmium complexes, OsHCl(CO)(PPh₃)₃ and OsH₂(CO)(PPh₃)₃, failed to react with the formazans under similar conditions. However green osmium formazan derivatives were obtained in small (ca. 5–10%) yield when the complexes Os(O₂CCF₃)₂(CO)(PPh₃)₂ or, preferably, OsH(O₂CCF₃)(CO)(PPh₃)₂ were employed. The yields were marginally improved (to ca. 20%) when dimethylformamide, a high boiling and more basic solvent, was used in place of 2-methoxyethanol.

An X-ray diffraction study performed on the green product obtained from the reaction of RuH₂(CO)(PPh₃)₃ and 1,3,5-

(35) For example: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273.

(36) Supplementary material.

Table III. Derived Parameters for Rigid Group Atoms

ATOM	X	Y	Z	H.A. ²	ATOM	X	Y	Z	H.A. ²
C(20)	0.36221(31)	0.03200(19)	-0.42290(31)	2.91(18)	C(20)*	-0.05309(40)	-0.02432(29)	0.14876(31)	5.95(29)
C(21)	0.37265(34)	0.01276(23)	-0.44828(24)	3.93(21)	C(21)*	-0.08962(40)	0.02370(28)	0.14928(27)	4.94(25)
C(22)	0.41176(36)	-0.03366(25)	-0.49386(25)	4.31(23)	C(22)*	-0.12525(35)	0.04441(21)	0.08748(35)	3.72(20)
C(23)	0.44043(34)	-0.06086(20)	-0.43405(33)	4.19(22)	C(23)*	-0.12435(37)	0.01711(27)	0.02516(27)	4.56(23)
C(24)	0.42999(34)	-0.04162(23)	-0.36866(26)	4.07(22)	C(24)*	-0.08782(42)	-0.03091(27)	0.02464(31)	5.48(27)
C(25)	0.39088(34)	0.00480(24)	-0.36309(23)	3.54(20)	C(25)*	-0.05219(39)	-0.05163(22)	0.08645(41)	5.84(29)
C(26)	0.29655(38)	0.09370(28)	-0.32805(29)	3.55(21)	C(26)*	-0.23716(49)	0.07596(31)	0.19715(47)	7.30(33)
C(27)	0.34080(33)	0.11402(28)	-0.27060(41)	5.57(26)	C(27)*	-0.25817(49)	0.07871(41)	0.26361(54)	9.12(39)
C(28)	0.32339(44)	0.10507(33)	-0.20370(32)	7.34(34)	C(28)*	-0.23280(68)	0.11958(53)	0.30036(40)	11.99(50)
C(29)	0.26173(49)	0.07579(35)	-0.19425(31)	7.55(35)	C(29)*	-0.18642(77)	0.15771(45)	0.28665(59)	25.7(12)
C(30)	0.21748(36)	0.05547(31)	-0.25170(44)	7.03(33)	C(30)*	-0.16540(59)	0.15496(36)	0.22019(64)	20.26(89)
C(31)	0.23489(35)	0.06442(28)	-0.31860(35)	4.60(24)	C(31)*	-0.19078(46)	0.11409(37)	0.17544(39)	4.13(22)
C(32)	0.39602(29)	0.14193(23)	-0.41108(33)	3.18(19)	C(32)*	-0.09439(38)	0.15233(36)	0.07775(45)	4.95(24)
C(33)	0.38976(30)	0.19268(26)	-0.38487(35)	4.49(23)	C(33)*	-0.03722(49)	0.13645(28)	0.04226(41)	6.08(28)
C(34)	0.44833(40)	0.22748(19)	-0.38170(37)	5.45(26)	C(34)*	0.02193(40)	0.16988(41)	0.03875(46)	7.21(33)
C(35)	0.51316(33)	0.21153(25)	-0.40475(39)	5.73(28)	C(35)*	0.02391(51)	0.21919(37)	0.07073(57)	8.69(41)
C(36)	0.51943(28)	0.16079(27)	-0.43096(36)	4.93(24)	C(36)*	-0.03326(70)	0.23506(31)	0.10621(59)	17.13(85)
C(37)	0.46086(35)	0.12598(19)	-0.43413(32)	3.92(20)	C(37)*	-0.09241(54)	0.20164(42)	0.10972(53)	14.37(62)
C(38)	0.12915(38)	0.09941(25)	-0.68118(31)	3.68(20)	C(38)*	-0.38425(36)	0.09605(23)	-0.16292(28)	3.23(19)
C(39)	0.15970(36)	0.04914(26)	-0.68017(30)	4.31(22)	C(39)*	-0.44487(33)	0.10451(25)	-0.21217(37)	5.41(27)
C(40)	0.15319(40)	0.01891(22)	-0.74073(39)	5.29(26)	C(40)*	-0.45560(32)	0.07360(30)	-0.27209(32)	6.12(28)
C(41)	0.11613(44)	0.03895(30)	-0.80230(30)	6.36(29)	C(41)*	-0.40572(40)	0.03422(27)	-0.28276(28)	4.96(24)
C(42)	0.08558(42)	0.08921(32)	-0.80332(31)	7.92(35)	C(42)*	-0.34510(34)	0.02576(23)	-0.23352(35)	4.67(23)
C(43)	0.09209(40)	0.11944(23)	-0.74276(40)	6.32(29)	C(43)*	-0.33436(29)	0.05668(25)	-0.17360(29)	3.88(20)
C(44)	0.13419(37)	0.20522(20)	-0.63339(34)	3.41(19)	C(44)*	-0.36784(48)	0.21384(31)	-0.18960(36)	8.30(37)
C(45)	0.08277(32)	0.24358(29)	-0.62301(36)	5.26(25)	C(45)*	-0.37717(39)	0.20493(21)	-0.12031(38)	3.47(20)
C(46)	0.09070(38)	0.29484(25)	-0.64689(40)	6.50(29)	C(46)*	-0.39233(40)	0.24698(28)	-0.07812(28)	4.45(23)
C(47)	0.15004(44)	0.30774(21)	-0.68115(39)	6.07(28)	C(47)*	-0.39816(43)	0.29793(23)	-0.10522(41)	5.73(27)
C(48)	0.20145(35)	0.26939(30)	-0.69153(37)	5.95(29)	C(48)*	-0.38884(48)	0.30684(26)	-0.17452(44)	7.46(33)
C(49)	0.19353(33)	0.21813(25)	-0.66765(37)	4.83(24)	C(49)*	-0.37368(53)	0.26480(38)	-0.21671(30)	10.34(47)
C(50)	0.03721(33)	0.12894(31)	-0.58155(38)	4.58(23)	C(50)*	-0.46270(29)	0.12828(27)	-0.05627(34)	3.07(19)
C(51)	0.00825(42)	0.16113(25)	-0.53366(37)	5.04(25)	C(51)*	-0.51127(38)	0.16839(19)	-0.04492(36)	5.15(25)
C(52)	-0.06125(44)	0.15122(33)	-0.51641(38)	6.61(30)	C(52)*	-0.57715(34)	0.15615(25)	-0.02111(38)	5.87(28)
C(53)	-0.10180(35)	0.16911(39)	-0.54705(50)	8.80(41)	C(53)*	-0.59447(31)	0.10381(30)	-0.00865(37)	4.32(23)
C(54)	-0.07284(48)	0.07691(31)	-0.59494(48)	10.43(45)	C(54)*	-0.54590(41)	0.06371(21)	-0.02001(39)	6.37(30)
C(55)	-0.00333(49)	0.08683(29)	-0.61219(37)	6.83(30)	C(55)*	-0.48002(36)	0.07594(23)	-0.04382(38)	5.87(28)

RIGID GROUP PARAMETERS

GROUP	A ^a	Y ^c	Z ^c	DELTA ^b	EPSILON	ETA
PH-1	0.40132(21)	-0.01443(16)	-0.42847(21)	-2.5534(42)	-2.7640(33)	1.6506(43)
PH-2	0.27914(28)	0.08474(19)	-0.26115(27)	2.1446(50)	2.8566(45)	-1.5586(48)
PH-3	0.45459(25)	0.17673(17)	-0.40792(21)	-2.4839(42)	2.6577(42)	0.0629(45)
PH-4	0.12264(24)	0.06918(20)	-0.74174(25)	0.6084(52)	2.6906(43)	1.1758(51)
PH-5	0.14211(26)	0.25648(19)	-0.65727(22)	-1.8780(48)	2.6556(46)	0.4013(48)
PH-6	-0.03229(30)	0.11902(21)	-0.56430(26)	-3.2541(65)	2.4743(51)	-2.6683(63)
PH-1*	-0.08872(24)	-0.00361(18)	0.08696(25)	-2.7960(52)	2.5699(41)	1.8904(54)
PH-2*	-0.21179(37)	0.11684(28)	0.24190(35)	-0.5819(76)	-3.0270(70)	-1.3090(60)
PH-3*	-0.03524(36)	0.18576(25)	0.07424(30)	0.5502(81)	-2.5035(64)	2.9544(72)
PH-4*	-0.39498(24)	0.06514(17)	-0.22284(23)	-2.1094(42)	-2.9393(39)	2.1597(41)
PH-5*	-0.38300(25)	0.25589(21)	-0.14741(27)	-0.0423(78)	2.2516(47)	-1.3367(84)
PH-6*	-0.52859(26)	0.11605(19)	-0.03246(22)	-2.9014(41)	3.1197(44)	-2.6824(41)

^a x_c , y_c , and z_c are the fractional coordinates of the origin of the rigid group. ^b The rigid group orientation angles δ , ϵ , and η (radians) have been defined previously: La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.* 1965, 18, 511.

triphenylformazan in 2-methoxyethanol establishes this material as the cyclometalated species $\text{Ru}((o\text{-C}_6\text{H}_4\text{N}=\text{NC}(\text{Ph})=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$. Spectroscopic correspondence implies a similar formulation for the other Ru and Os products.

Description of the Structure. In the immediate coordination sphere and also in the formazan moiety the two crystallographically independent molecules of $\text{Ru}((o\text{-C}_6\text{H}_4\text{N}=\text{NC}(\text{Ph})=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$ show almost identical structure as diagramed in Figures 1 and 2 and as documented in Tables V (bond distances), VI (bond angles), VII (least-squares planes), and VIII (dihedral angles between least-squares planes). The ruthenium ions are both six-coordinate with two trans-directed phosphine ligands. Both the average Ru-P separation (2.384 (5) Å)³⁷ and the average Ru-C(CO) sep-

aration (1.83 (1) Å) are similar to those found in a related complex, $\text{RuH}(\text{PhN}=\text{CH}=\text{NPh})(\text{CO})(\text{PPh}_3)_2$.³⁸ The Ru-C(aryl) bonds average 2.091(9) Å and may be responsible for lengthening the trans Ru-N bonds relative to the cis Ru-N bonds (2.163 (7) Å compared with 2.02 (1) Å, respectively); however this asymmetry may be intrinsic in the stereochemical requirements of the formazan chelating ring. There are very few structures containing Ru-N bonds of this type available for comparison. However, in the above-mentioned structure³⁸

(37) The standard deviation in parentheses for averaged parameters is the larger of that calculated from the scatter of values about their mean and of that derived for an individual parameter from the inverse least-squares matrix.

(38) Brown, L. D.; Robinson, S. D.; Sahajpal, A.; Ibers, J. A. *Inorg. Chem.* 1977, 16, 2728.

Table V. Selected Bond Distances (Å) for Ru(*o*-C₆H₄)N=NC(Ph)=NNPh)(CO)(PPh₃)₂^a

atoms	dist	dist	atoms	dist	dist
Ru-C(1)	2.094 (9)	2.087 (9)	C(8)-C(9)	1.38 (1)	1.38 (1)
Ru-N(1)	2.164 (7)	2.161 (7)	C(8)-C(13)	1.40 (1)	1.40 (1)
Ru-N(3)	2.011 (7)	2.030 (7)	C(9)-C(10)	1.37 (1)	1.39 (1)
Ru-C(56)	1.839 (9)	1.823 (10)	C(10)-C(11)	1.33 (2)	1.36 (2)
Ru-P(1)	2.379 (3)	2.381 (3)	C(11)-C(12)	1.37 (2)	1.33 (2)
Ru-P(2)	2.390 (3)	2.385 (3)	C(12)-C(13)	1.41 (2)	1.43 (1)
N(1)-N(2)	1.308 (9)	1.312 (9)	C(14)-C(15)	1.36 (1)	1.36 (1)
N(1)-C(14)	1.42 (1)	1.41 (1)	C(14)-C(19)	1.39 (1)	1.35 (1)
N(2)-C(7)	1.33 (1)	1.35 (1)	C(15)-C(16)	1.39 (1)	1.39 (2)
C(7)-N(3)	1.38 (1)	1.36 (1)	C(16)-C(17)	1.35 (1)	1.34 (1)
C(7)-C(8)	1.46 (1)	1.47 (1)	C(17)-C(18)	1.36 (1)	1.34 (1)
N(3)-N(4)	1.304 (9)	1.295 (9)	C(18)-C(19)	1.40 (1)	1.40 (2)
N(4)-C(6)	1.41 (1)	1.41 (1)	P(1)-C(20)	1.835 (6)	1.829 (6)
C(1)-C(6)	1.42 (1)	1.41 (1)	P(1)-C(26)	1.824 (7)	1.815 (8)
C(1)-C(2)	1.40 (1)	1.42 (1)	P(1)-C(32)	1.825 (6)	1.823 (8)
C(2)-C(3)	1.39 (1)	1.38 (1)	P(2)-C(38)	1.836 (7)	1.830 (6)
C(3)-C(4)	1.37 (1)	1.36 (1)	P(2)-C(44)	1.838 (6)	1.821 (6)
C(4)-C(5)	1.38 (1)	1.37 (1)	P(2)-C(50)	1.836 (7)	1.830 (6)
C(5)-C(6)	1.39 (1)	1.39 (1)	C(56)-O(1)	1.16 (1)	1.18 (1)

^a The first entry is for molecule 1; the second is the equivalent parameter for molecule 2.

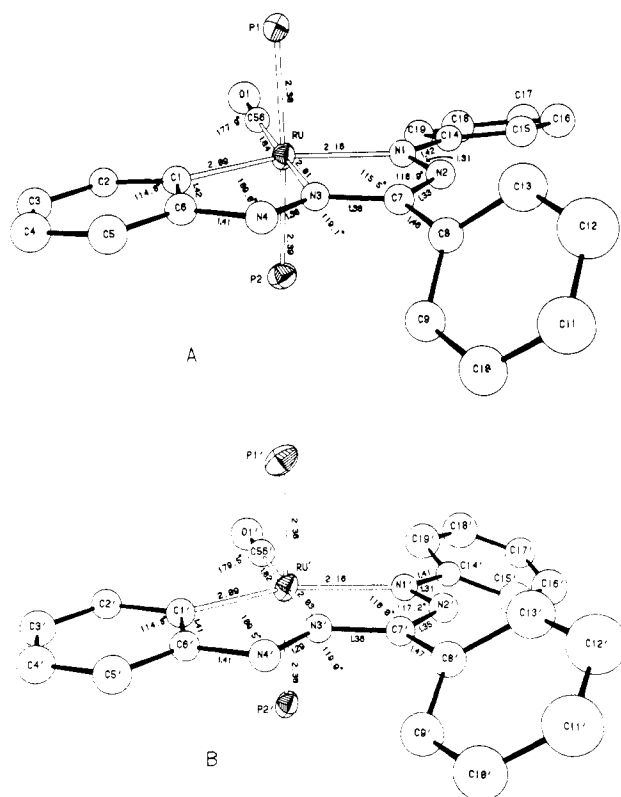
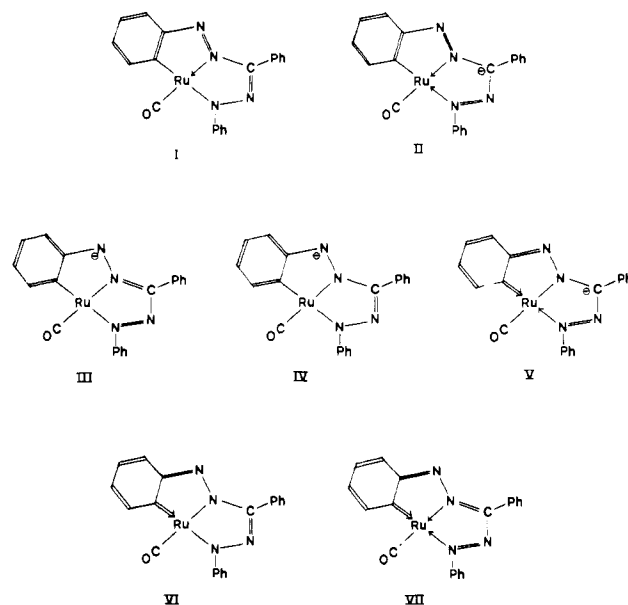


Figure 1. Coordination sphere and the triphenylformazan moiety. Hydrogen atoms on phenyl groups are omitted for clarity. Thermal ellipsoids are drawn at the 35% probability level. The atom labeling system and some metrical details are also included. Molecule 1 is shown in A; molecule 2 is shown in B.

the Ru-N bond trans to the carbonyl ligand is more than 0.18 Å longer than the corresponding bond in the present structure.

It is only in the orientation of the phenyl rings that the differences between molecules 1 and 2 become visually apparent (see Figures 1 and 2 and Table VIII). For the triphenylformazan moiety, with respect to the 7-membered chelating ring (plane Coord), phenyl rings B' and C' adopt a slightly different orientation. The differences in orientation of the phosphine phenyl rings are best appreciated in the stereodiagram of Figure 2. These small differences in orientation reflect subtle differences in the packing environments

Chart I



around molecules 1 and 2. The molecules themselves are very well separated with only five contacts less than 3.50 Å among the nonhydrogen atoms; the shortest contact C(35)···N(2) is 3.41 Å. Figure 3 shows a packing diagram of the molecules in the cell.

Bonding in the Ru(*o*-C₆H₄)N=NC(Ph)=NNPh) Moiety. The pattern of bond lengths in the formazan chelate indicates a highly delocalized bonding. A number of resonance structures, some of which are more unlikely than others, are shown in Chart I. Since an Ru-C < carbenoid bond of 1.908 (5) Å has been observed for the complex RuCl(PEt₃)₂CN-(Ar)(CH₂)₂N(C₆H₃Me-4)³⁹ and since Ru-C(aryl) bond lengths have been observed in the range 1.994 (5)³⁹ to 2.16 (1) Å,⁴⁰ there is little evidence for significant carbenoid character in the Ru-C(aryl) bonds (average Ru-C = 2.091 Å). Thus, resonance forms V-VII (especially VII which also

(39) Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Chem. Commun.* 1977, 196.

(40) Gregory, U. A.; Ibekwe, S. D.; Kilbourn, B. T.; Russell, D. R. *J. Chem. Soc. A* 1971, 1118.

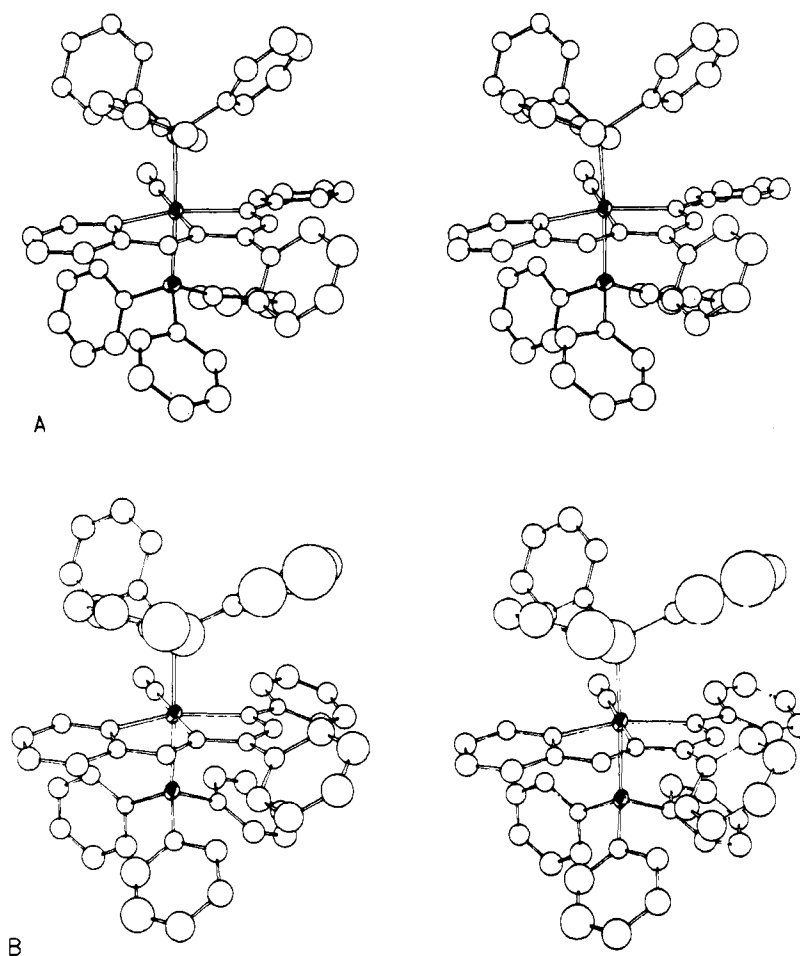


Figure 2. Stereodiagram of $\text{Ru}((o\text{-C}_6\text{H}_4)\text{N}=\text{NC}(\text{Ph})=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 35% probability level. Molecule 1 is shown in A; molecule 2 is shown in B.

Table VI. Selected Bond Angles (Deg) for $\text{Ru}((o\text{-C}_6\text{H}_4)\text{N}=\text{NC}(\text{Ph})=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$ ^a

atoms	angle	angle	atoms	angle	angle
P(1)–Ru–P(2)	176.5 (1)	177.8 (1)	C(5)–C(6)–C(1)	123.6 (8)	123.1 (9)
C(56)–Ru–N(3)	176.2 (3)	177.6 (3)	C(5)–C(6)–N(4)	115.9 (8)	116.0 (9)
C(1)–Ru–N(1)	152.2 (3)	151.9 (3)	C(1)–C(6)–N(4)	120.4 (8)	120.9 (8)
C(1)–Ru–N(3)	76.8 (3)	77.1 (3)	C(6)–N(4)–N(3)	109.0 (7)	109.5 (7)
N(3)–Ru–N(1)	75.4 (3)	75.0 (3)	N(4)–N(3)–C(7)	119.1 (7)	119.9 (7)
N(1)–Ru–C(56)	105.4 (3)	105.5 (3)	N(3)–C(7)–N(2)	115.5 (8)	116.0 (8)
C(56)–Ru–C(1)	102.4 (4)	102.5 (4)	N(3)–C(7)–C(8)	124.6 (8)	125.9 (8)
P(1)–Ru–C(56)	87.7 (2)	90.5 (3)	N(2)–C(7)–C(8)	119.8 (8)	118.1 (8)
P(2)–Ru–C(56)	92.4 (3)	90.5 (3)	C(7)–N(2)–N(1)	118.9 (7)	117.2 (7)
P(1)–Ru–C(1)	88.6 (2)	89.6 (2)	N(2)–N(1)–C(14)	112.3 (7)	113.0 (7)
P(2)–Ru–C(1)	87.9 (2)	88.2 (2)	C(7)–C(8)–C(5)	122.7 (9)	123.5 (9)
P(1)–Ru–N(3)	88.5 (2)	88.1 (2)	C(7)–C(8)–C(13)	115.9 (5)	119 (1)
P(2)–Ru–N(3)	91.3 (2)	91.9 (2)	C(9)–C(8)–C(13)	117.7 (9)	118 (1)
P(2)–Ru–N(1)	91.8 (2)	92.0 (2)	C(8)–C(9)–C(10)	121 (1)	119 (1)
P(2)–Ru–N(1)	91.6 (2)	89.6 (2)	C(9)–C(10)–C(11)	121 (1)	120 (1)
Ru–C(56)–O(1)	177.9 (8)	179.5 (8)	C(10)–C(11)–C(12)	119 (1)	122 (1)
Ru–C(1)–C(2)	135.1 (7)	135.3 (7)	C(11)–C(12)–C(13)	120 (1)	120 (1)
Ru–C(1)–C(6)	109.8 (6)	109.8 (6)	C(12)–C(13)–C(8)	119 (1)	119 (1)
Ru–N(3)–N(4)	123.6 (5)	122.7 (6)	N(1)–C(14)–C(15)	122.9 (8)	123.7 (8)
Ru–N(3)–C(7)	117.1 (6)	117.4 (6)	N(1)–C(14)–C(19)	118.1 (8)	120.3 (9)
Ru–N(1)–N(2)	113.0 (5)	114.2 (5)	C(15)–C(14)–C(19)	118.9 (9)	116 (1)
Ru–N(1)–C(14)	134.7 (6)	132.7 (6)	C(14)–C(15)–C(16)	121 (1)	122 (1)
C(6)–C(1)–C(2)	114.8 (8)	114.8 (8)	C(15)–C(16)–C(17)	120 (1)	121 (1)
C(1)–C(2)–C(3)	121.4 (9)	121.6 (9)	C(16)–C(17)–C(18)	120 (1)	119 (1)
C(2)–C(3)–C(4)	122 (1)	120 (1)	C(17)–C(18)–C(19)	119 (1)	120 (1)
C(3)–C(4)–C(5)	120 (1)	120 (1)	C(18)–C(19)–C(14)	120 (1)	122 (1)
C(4)–C(5)–C(6)	119 (1)	118.9 (9)			

^a The first entry is for molecule 1; the second is the equivalent parameter for molecule 2.

involves a six-coordinate Ru(0) species) are undoubtedly minor contributors to a delocalized bonding arrangement. Fur-

thermore both Ar–N bond lengths are identical and are typical of those in mildly conjugated aromatic systems such as ace-

Table VII. Least-Squares Planes for $\text{Ru}((o\text{-C}_6\text{H}_4\text{N}=\text{NC}(\text{Ph})=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$

name	coefficients $Ax + By + Cz - D = 0^a$				displacement ^b of atoms defining plane				other atoms displacement			
	A	B	C	D								
Fmzn	11.741	-6.848	12.376	-4.509	N(1) -002 (7)	N(3) 002 (7)	N(1) -006 (7)	N(2) 004 (9)			Ru 060	
Fmzn'	12.699	-6.173	11.506	-4.303	N(1) 001 (7)	N(3) -001 (7)	C(7) 002 (8)	N(2) -001 (7)			Ru 091	
coord	11.527	-6.856	12.585	-4.646	N(1) 006 (7)	N(3) -025 (7)	C(1) -003 (9)	C(6) 002 (9)			Ru 039	
coord'	12.864	-5.745	11.422	-4.282	N(1) -020 (9)	N(3) 021 (7)	C(1) 030 (9)	C(6) 025 (9)	N(4) 024 (7)	N(2) 011 (7)		
Ph-A	12.103	-8.007	11.622	-4.087	C(1) 021 (9)	C(2) -013 (9)	C(3) 001 (10)	C(4) 002 (11)	C(5) 011 (10)	N(2) -001 (7)	Ru 077	
Ph-A'	13.097	-4.230	11.473	-4.074	C(1) -019 (9)	C(2) 014 (9)	C(3) 002 (10)	C(4) -012 (10)	C(5) 003 (10)			
Ph-B	18.494	-1.664	-2.048	4.622	C(8) -006 (9)	C(9) 015 (10)	C(10) -020 (1)	C(11) 013 (13)	C(12) 000 (14)			
Ph-B'	18.232	-2.853	2.927	-5.802	C(8) -000 (9)	C(9) 002 (10)	C(10) -000 (12)	C(11) -007 (14)	C(12) 010 (14)			
Ph-C	10.398	-12.491	11.410	-5.041	C(14) -004 (9)	C(15) -007 (10)	C(16) 019 (11)	C(17) -011 (11)	C(18) -006 (11)			
Ph-C'	9.164	0.571	15.484	-1.765	C(14) 013 (8)	C(15) -002 (11)	C(16) -017 (12)	C(17) 010 (11)	C(18) 010 (12)			

^a The plane is in crystal coordinates as defined by: Hamilton, W. C. *Acta Crystallogr.* 1961, 14, 185. ^b The displacement in Å is generated by placing a decimal point prior to the first digit.

Table VIII. Dihedral Angles (Deg) between Selected Least-Squares Planes^a

	Fmzn ^b	coord	Ph-A	Ph-B	Ph-C
Fmzn	(4.0) ^c				
Fmzn'					
coord	0.9	(5.7)			
coord'	1.1				
Ph-A	3.5	4.1	(9.9)		
Ph-A'	4.6	3.5			
Ph-B	48.3	49.1	46.6	(7.4)	
Ph-B'	37.0	36.4	35.8		
Ph-C	13.9	13.7	11.5	52.7	(32.4)
Ph-C'	21.6	21.3	19.4	52.6	

^a See Table VII for definition of planes. ^b The lower entry of each pair is for molecule 2; the upper for molecule 1. ^c The entries in parentheses on the diagonal are the dihedral angles between a plane of molecule 1 and its equivalent in molecule 2.

tanilide (N-C(aryl) = 2.426 (12) Å).

The N-N bonds are very similar to those observed for a 1,5-coordinated formazan complex of palladium(II)²⁴ and of nickel(II).²⁵ The bond length between the formazan carbon atom C(7) and phenyl ring B appears to be significantly shorter than the value of 1.50 Å observed between an aromatic sp² carbon atom and a phenyl group such as in a porphyrin compound.⁴¹ Thus, a substantial contribution of resonance form II is implied with delocalization of the negative charge onto the phenyl ring. Because we find little evidence for the carbeneoid resonance forms, form II assumes importance similar to form I since the two chemically distinct pairs of N-N bonds have identical lengths. Resonance form III with a negatively charged N atom and, particularly, form IV which implies Ru(III) are far less likely. The apparent small difference between the two C-N bonds (C(7)-N(3) and C(7)-N(2)) is not statistically significant, so it is not possible to assess the contribution of form III.

Mechanism of Formation. In an attempt to elucidate the reaction pathway leading to formation of the green cyclometalated products, a series of reactions were performed with use of milder reaction conditions (<100 °C, steambath) and/or shorter reaction times (ca. 5–20 min). The dark colored mixtures obtained were shown by TLC and ³¹P NMR techniques to contain three components—a green complex similar to those described above and two minor products, one pink and one purple. The mixture derived from $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ and $\text{PhN}=\text{NCH}=\text{NNHPh}$ gave the highest proportion of pink and purple minor components and was therefore selected for further investigation. Chromatographic separation on a 10 × 2.5 cm column of silica gel using dichloromethane and 2:1 ethanol/dichloromethane as eluants gave, in order of removal from the column, pink, green, and purple fractions. The pink material, which was obtained only in very small yield (ca. 5%), slowly converted to the purple product in solution. The latter, on heating in boiling 2-methoxyethanol for ca. 30 min, was transformed into a green product, which was shown spectroscopically to be identical with the green complex described above.

The ³¹P NMR spectrum of each component consists of a singlet. Chemical shift values (δ(P) 34.39 and 42.79, respectively) for the green and purple products are consistent with the presence of a trans pair of triphenylphosphine ligands in each complex. The ³¹P resonance for the pink component occurs at higher field (δ(P) 22.43) which we take as an indication of the presence of a symmetrically coordinated N¹,N⁵-bound formazan ligand trans to the triphenylphosphine ligands. The infrared spectra of the pink and purple complexes

(41) Hoard, J. L. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; pp 317.

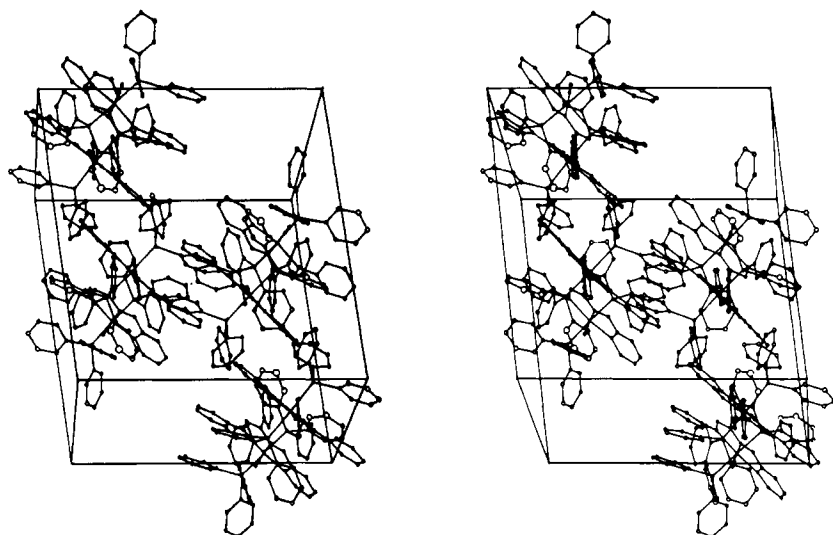
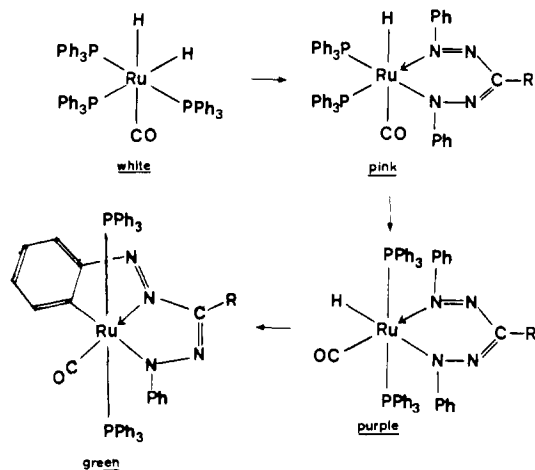


Figure 3. Stereodiagram of the unit cell of $\text{Ru}((o\text{-C}_6\text{H}_4)\text{N}=\text{NC}(\text{Ph})=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$. This view down the b axis illustrates the pronounced pseudo B centering.

Scheme I



differ significantly only in the position of the $\nu(\text{CO})$ absorption (1973, 1960 against 1935 cm^{-1}). They both show bands consistent with the presence of N^1, N^5 -chelate formazan ligands²⁸ and are simpler than that of the corresponding green product. In particular the latter product displays additional strong absorptions at 1195, 1250, and 1280 cm^{-1} . Neither spectrum shows evidence for the presence of a hydride ligand. However, the proton NMR spectrum of the purple product does display a high-field triplet signal ($\tau\ 19.7$, $^2J(\text{PH})_{\text{cis}} = 20\text{ Hz}$) indicative of a hydride cis to a pair of equivalent triphenylphosphine ligands. On the basis of this evidence and the results of the X-ray diffraction study, we conclude that the overall reaction sequence being observed in these systems follows the path indicated in Scheme I and that the structures of the pink and purple intermediates are as indicated therein.

The conversion of the purple intermediate to the green final product affords the first example of an N^1, N^5 -coordinated formazan ligand rearranging to adopt N^1, N^4 -coordination. It thus substantiates an earlier but hitherto unsupported suggestion that some of the many tridentate ligands derived from functionally substituted formazans may also choose N^1, N^4 -coordination in order to facilitate attachment at the third donor site.^{30,31}

The ease of isolation of the pink and purple intermediates is dependent upon the nature of the formazan substituent, R , and increases in the sequence $\text{Ph} < \text{Me} \ll \text{H}$. The acidity of the formazans measured in ethanol increases⁴² in the same order ($\text{p}K_{\text{a}}$ values > 19.0 , 18.3 , and 16.5 for $\text{R} = \text{Ph}$, Me , and H , respectively). It seems probable that the rate of formation of the pink complexes, and hence their purple isomers, are dependent upon the acidity of the formazan concerned, whereas the subsequent conversion to the green cyclometalated product is not. Thus only the most acidic formazan $\text{PhN}=\text{NCH}=\text{NNHPh}$ reacts under conditions sufficiently mild to permit facile isolation of the pink and purple intermediates before they are able to cyclometalate to the corresponding green products. Less acidic formazans ($\text{R} = \text{Ph}$ or Me) require more forcing conditions or prolonged reaction times to yield the corresponding pink and purple intermediate complexes. These conditions are such that the intermediate complexes undergo cyclometalation to the final green products before they have an opportunity to accumulate in the reaction mixture.

Acknowledgment. This research was supported in part by the U.S. National Science Foundation (Grant CHE76-10335).

Registry No. $\text{Ru}((o\text{-C}_6\text{H}_4)\text{N}=\text{NC}(\text{Ph})=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$, 77123-39-8; $\text{Ru}((o\text{-C}_6\text{H}_4)\text{N}=\text{NC}(\text{Me})=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$, 77110-88-4; $\text{Ru}((o\text{-C}_6\text{H}_4)\text{N}=\text{NCH}=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$, 77110-89-5; $\text{Ru}((o\text{-C}_6\text{H}_4)\text{N}=\text{NC}(\text{Ph})=\text{NNPh})(\text{CO})(\text{AsPh}_3)_2$, 77110-90-8; $\text{Os}((o\text{-C}_6\text{H}_4)\text{N}=\text{NC}(\text{Ph})=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$, 77110-91-9; $\text{Os}((o\text{-C}_6\text{H}_4)\text{N}=\text{NC}(\text{Me})=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$, 77110-92-0; $\text{Os}((o\text{-C}_6\text{H}_4)\text{N}=\text{NCH}=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$, 77123-40-1; *cis*- $\text{Ru}(\text{PhN}=\text{NCH}=\text{NNPh})\text{H}(\text{CO})(\text{PPh}_3)_2$, 77123-41-2; *trans*- $\text{Ru}(\text{PhN}=\text{NCH}=\text{NNPh})\text{H}(\text{CO})(\text{PPh}_3)_2$, 77171-63-2; $\text{RuHCl}(\text{CO})(\text{PPh}_3)_2$, 16971-33-8; $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$, 25360-32-1; $\text{RuH}_2(\text{CO})(\text{AsPh}_3)_3$, 77170-95-7; $\text{OsH}(\text{O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2$, 63701-16-6; $\text{Os}(\text{O}_2\text{CCF}_3)_2(\text{CO})(\text{PPh}_3)_2$, 38596-63-3.

Supplementary Material Available: Table IV, idealized hydrogen atom parameters, and a listing of calculated and observed structure amplitudes (31 pages). Ordering information is given on any current masthead page.

(42) Gill, J. B.; Irving, H. M. N. H.; Prescott, A. J. *Chem. Soc., Perkin Trans. 2* 1977, 1683.