changeover has been noticed for these metals for the displacement of flexible chelate rings bonding through S by phosphines and phosphites[17] and for solvent-exchange processes in the first transition series.[19] In both cases the changeover correlates with metal size and was confirmed by trends in the activation volume. High-pressure kinetic studies are underway to throw more light on the intimate mechanism of the phenanthroline system. Furthermore, Scheme I is a possible explanation for the enhancement of the ligand-independent term in the indenyl system of Huggins et al.[6] CO has, in general, the effect of increasing the rate of substitution as expected when a reverse reaction is present. The replacement of the cyclopentadienyl ligand by an indenyl ligand lowers the activation energy barrier for the forward, as well as the reverse, associative reaction paths.

Conclusions

We have shown that the reverse reaction of M(phen)-$(CO)_3L$ with CO makes the system more complicated than initially thought. Disregard of this possibility is likely to lead to false conclusions.

As shown in eq 5, the presence of a two-term rate law need not necessarily imply competing reactions but can be ascribed to the reverse reaction. The molybdenum system studied in this work appears to react via competing associative and dissociative pathways, but each case must be considered separately. Compounds that are stable in solution could well approach equilibrium via a purely associative mechanism, with eq 5 describing the observed rate constant.

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Volkswagen-Stiftung.

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[19] Merbach, A.: Ducommun, Y. In *Inorganic High Pressure Chemistry*: Kinetics *and Mechanisms*; van Eldik, R., Ed.; Elsevier: Amsterdam, 1986; Chapter 2.

Reactions of Transition-Metal σ-Acetylide Complexes. 14.[1] Cyclobutenyl, Butadienyl, and Allyl Complexes of Ruthenium Derived from 1,1-Dicyano-2,2-bis(trifluoromethyl)ethene. X-ray Structures of $Ru[\overline{C{=}CPhC(CF_3)_2C}(CN)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$, $Ru[C({=}C(CN)_2)CX{=}C(CF_3)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$ (X = Me, Ph), and $Ru[\eta^3\text{-}C(CF_3)_2CPhC{=}C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)$

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Received April 24, 1989

Reactions between $Ru(C_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$ or $Ru(C_2Ph)(L)_2(\eta\text{-}C_5H_5)$ (L_2 = $(PPh_3)_2$, dppe, $(CO)(PPh_3)$) and $(CF_3)_2C{=}C(CN)_2$ gave the corresponding σ-cyclobutenyl complexes, of which $Ru[\overline{C{=}CPhC(CF_3)_2C}(CN)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$ (**1g**) was fully characterized by X-ray crystallography. Thermal isomerization of the dppe and $(CO)(PPh_3)$ complexes to the σ-buta-1,3-dien-2-yl derivatives occurred; under CO, two isomers of $Ru[C({=}C(CN)_2)CMe{=}C(CF_3)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$ were formed. The X-ray structures of one of these (**2h**), and the phenyl analogue (**2g**), were determined. The allyls $Ru[\eta^3\text{-}C(CF_3)_2CXC{=}C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)$ (X = Me (**3d**), Ph (**3g**)) were obtained thermally or photochemically; the structure of **3g** was also determined, thus completing the series σ-cyclobutenyl, σ-butadienyl, η^3-allyl derived from the same metal/ligand combinations. Crystal data for **1g**: orthorhombic, space group $P2_12_12_1$, a = 10.409 (2) Å, b = 16.227 (3) Å, c = 20.000 (3) Å, Z = 4; 2851 data were refined to R = 0.040, R_w = 0.041. Crystal data for **2g**: monoclinic, space group $P2_1/n$, a = 14.942 (1) Å, b = 13.413 (2) Å, c = 16.928 (6) Å, β = 97.02 (1)°, Z = 4; 3659 data were refined to R = 0.045, R_w = 0.059. Crystal data for **2h**: monoclinic, space group $C2/c$, a = 22.237 (4) Å, b = 18.648 (5) Å, c = 17.731 (3) Å, β = 124.93 (2)°, Z = 8; 3076 data were refined to R = 0.039, R_w = 0.042. Crystal data for **3g**: monoclinic, space space $P2_1/n$, a = 13.804 (3) Å, b = 17.257 (2) Å, c = 13.957 (3) Å, β = 98.49 (2)°, Z = 4; 2922 data were refined to R = 0.055, R_w = 0.062.

Introduction

We have recently described reactions between 1,1-dicyano-2,2-bis(trifluoromethyl)ethene, $(NC)_2C{=}C(CF_3)_2$ (dcfe), and substituted acetylide complexes containing $W(CO)_3(\eta\text{-}C_5H_5)$, $Mn(CO)_3(dppe)$, or $Fe(CO)_2(\eta\text{-}C_5H_5)$ groups, to give the σ-cyclobutenyl complexes (**1a**–**c**, Scheme I).[2] The reaction between **1a** and $Me_3NO{\cdot}2H_2O$ afforded the hydrolysis product $W[\overline{NH{=}C(OH)C(CN){=}C}CPh{=}C(CF_3)_2](CO)_2(\eta\text{-}C_5H_5)$, formed by addition of

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[1] Part 13: Bruce, M. I.; Liddell, M. J.; Tiekink, E. R. T. *J. Organomet. Chem.* 1988, *352*, 199.

[2] Bruce, M. I.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *Organometallics* 1988, *7*, 343.

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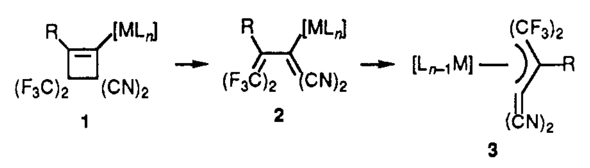
Scheme I



	R	ML_n	ML_{n-1}
a	Ph	$W(CO)_3(\eta\text{-}C_5H_5)$	$W(CO)_2(\eta\text{-}C_5H_5)$
b	Ph	$Mn(CO)_3(dppe)$	
c	Ph	$Fe(CO)_2(\eta\text{-}C_5H_5)$	
d	Me	$Ru(PPh_3)_2(\eta\text{-}C_5H_5)$	$Ru(PPh_3)(\eta\text{-}C_5H_5)$
e	Ph	$Ru(PPh_3)_2(\eta\text{-}C_5H_5)$	
f	Ph	$Ru(dppe)(\eta\text{-}C_5H_5)$	
g	Ph	$Ru(CO)(PPh_3)(\eta\text{-}C_5H_5)$	$Ru(PPh_3)_2(\eta\text{-}C_5H_5)$
h	Me	$Ru(CO)(PPh_3)(\eta\text{-}C_5H_5)$	

H_2O to one of the CN groups of the related σ-buta-1,3-dien-2-yl precursor, instead of the expected allyl complex **3a**. The σ-cyclobutenyl complexes were relatively stable toward isomerization by ring opening to the butadienyls **2**, and we have followed up this study with an investigation of related reactions of ruthenium-containing complexes, reported herein. This afforded a series of cyclobutenyl, butadienyl, and allyl complexes; X-ray studies of four of these are also described.

Results

Complexes. (a) Cyclobutenyls. The reaction of $Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)$ with $(NC)_2C{=}C(CF_3)_2$ in toluene or acetonitrile leads to precipitation of $Ru[\overline{C{=}CMeC(CF_3)_2C}(CN)_2](PPh_3)_2(\eta\text{-}C_5H_5)$ (**1d**) as a yellow powder. Complex **1d** was shown from ^1H NMR and microanalytical data to be a 1:1 adduct of $Ru(C{\equiv}CMe)(PPh_3)_2(\eta\text{-}C_5H_5)$ and $(NC)_2C{=}C(CF_3)_2$; in the EI mass spectrum a molecular ion was observed at m/z 944. The ^1H NMR spectrum has resonances at δ 0.53 (s), 4.64 (s), and 6.9–7.2 (m) ppm assigned to methyl, cyclopentadienyl, and phenyl groups, respectively. In the ^{13}C NMR spectrum resonances at δ 16.4 (s), 84.8 (s), 116.4 (s), 127.7–140.4 (m), and 149.6 (t, J(CP) = 4 Hz) ppm are assigned to methyl, cyclopentadienyl, cyano, phenyl, and Ru-bonded carbons, respectively; resonances of other carbons were not observed before the complex decomposed to an unidentified product, perhaps the butadienyl complex **2d**. In the infrared spectrum a very weak band at 2238 cm^{-1} is assigned to ν(CN) and is consistent with the formulation as a cyclobutenyl complex. The extended study we have made of cycloadducts obtained from transition-metal acetylides and cyanoolefins has led to the use of ν(CN) absorptions in the assignment of structural type, the intensities being as follows: cyclobutenyl, very weak; butadienyl, weak to medium; allyl, weak to strong. These assignments have proven to be more reliable as a guide to structure type than ν(C=C).[3] Other bands at 1572 m and 1270 vs, 1220 s, and 1197 s cm^{-1} are assigned to ν(C=C) and ν(CF), respectively.

A similar reaction between dcfe and $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$, carried out in acetonitrile, gave $Ru[\overline{C{=}CPhC(CF_3)_2C}(CN)_2](PPh_3)_2(\eta\text{-}C_5H_5)$ (**1e**); in benzene, a deep blue binuclear complex was obtained, which will be described elsewhere.[4] The dppe analogue **1f** was obtained from dcfe and $Ru(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$ in benzene. Both complexes formed yellow microcrystalline powders; **1f** was characterized by NMR signals at δ 4.71 (^1H) and 85.4 ppm (^{13}C) for the $\eta\text{-}C_5H_5$ group. Only C_α of the ring carbons was detected, at δ 178.6 ppm; the CN resonance was also weak, at δ 115.6 ppm. The instability of **1e** in solution prevented our obtaining NMR data. From the infrared spectra of complexes **1e** and **1f** they are both assigned cyclobutenyl structures, very weak ν(CN) bands being observed at 2239 and 2233 cm^{-1}, respectively.

As we have pointed out before, the fast-atom bombardment (FAB) mass spectra allow ready distinction between the isomeric cyclobutenyl and butadienyl formulations for these complexes.[2] Loss of dcfe from M^+ is possible in the former but is not observed in the latter. In the spectra of **1e** and **1f**, strong ions corresponding to $[M - dcfe]^+$ were found. However, in the case of **1d** the ring has greater stability toward fragmentation and loss of the triphenylphosphine ligands occurs preferentially, $[M - PPh_3]^+$ being a prominent high-mass ion.

Finally, replacement of one PPh_3 in **1e** by CO was achieved by leaving a solution of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ and dcfe under CO for several days, when white **1g** was formed in 63% yield. This complex was also obtained from dcfe and $Ru(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ in 84% yield. This complex has ν(CN) at 2240 vw cm^{-1} and ν(CO) at 1960 s cm^{-1} and C_5H_5 resonances at δ 5.02 (^1H) and 87.3 (^{13}C) ppm; other ^{13}C resonances were at δ 219.6 (CO) and 114.8 and 113.4 (CN) ppm. The FAB mass spectrum confirmed the expected cyclobutenyl formulation in containing the ions $[M - dcfe]^+$ and $[M - CO - dcfe]^+$.

(b) Butadienyls. Carbonylation (50 atm, 120 °C, 20 h) of **1d** gave two isomeric complexes, the minor isomer being identified as the buta-1,3-dien-2-yl derivative **2h** by an X-ray structural study (see below). The second isomer has virtually identical infrared, ^1H NMR, and mass spectra. The two forms are readily separable by chromatography and do not interconvert. Since the unit cell of the X-ray-characterized species **2h** contains both enantiomers related by a crystallographic center of inversion (see below), the major isomer is not one of these anticipated stereoisomers. From models it appears that the major isomer may be related to **2h** by rotation of the butadienyl ligand so that the two trifluoromethyl groups are in a sterically less demanding position. This rotation is restricted by the triphenylphosphine ligand and explains the lack of interconversion found at room temperature.

Conversion of **1f** and **1g** to the ring-opened isomers **2f** and **2g**, respectively, was achieved by heating solutions of the cyclobutenyls in xylene. In both cases, a mixture of products was purified by chromatography to give as the major components the butadienyl complexes in 20–30% yield. These were identified spectroscopically, having medium-intensity ν(CN) bands at ca. 2210 cm^{-1} in their infrared spectra, C_5H_5 signals at δ 4.30 and 4.61 ppm, and no ions at m/z 666 (**2f**) or 558 or 530 (**2g**), corresponding to loss of dcfe. The butadienyl formulation was also confirmed by an X-ray determination of the molecular structure of **2g**.

The ^1H NMR spectrum of **2f** contained a second C_5H_5 peak at δ 4.67 ppm, suggesting the presence of an isomer, present in about one-fourth of the amount of the major isomer. We have not been able to separate this product, either by extensive chromatography or by crystallization. We suggest it is related to the major product by restricted rotation of the butadienyl group.

(c) Allyls. Attempted conversion of **1d** to the corresponding butadienyl by heating in acetonitrile for several hours gave instead yellow crystals of Ru[η^3-C-

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(3) Bruce, M. I.; Humphrey, P. A.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1986**, *303*, 417.

(4) Bruce, M. I.; Hambley, T. W.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. Manuscript in preparation.

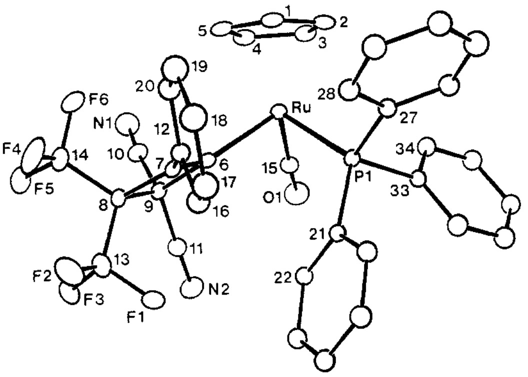

Figure 1. ORTEP view of $Ru[\overline{C{=}CPhC(CF_3)_2C}(CN)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$ (**1g**) showing the atom-labeling scheme. Atoms not otherwise indicated are carbons.

$(CF_3)_2CMeC{=}C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)$ (**3d**). Formation of this compound occurs via the acetonitrile complex $Ru[C({=}C(CN)_2)CMe{=}C(CF_3)_2](NCMe)(PPh_3)(\eta\text{-}C_5H_5)$, which was not isolated analytically pure but was characterized spectroscopically. The ^1H NMR spectrum had Me, CH_3CN, and C_5H_5 proton resonances at δ 1.11, 1.81, and 4.54 ppm, respectively, a molecular ion was observed in the FAB mass spectrum at m/z 723, and in the infrared spectrum weak ν(CN) modes were found at 2268 and 2238 cm^{-1}. This compound is presumably formed via an acetonitrile cyclobutenyl intermediate, related to the structurally characterized complex $Ru[\overline{C{=}CPhC(CF_3)_2C}(CN)_2](NCMe)(PPh_3)(\eta\text{-}C_5H_5)$.[4] Irradiation of the butadienyl **2g** (100-W high-pressure lamp, 24 h) gave the phenyl analogue **3g** in low yield. Elemental analyses of these two complexes revealed the loss of a PPh_3 or CO ligand, respectively, from the precursor, which was also confirmed by the ^1H NMR spectrum for **3d** and the infrared spectrum for **3g**. The ν(CN) modes were strengthened in these compounds, strong absorptions being found at 2220 cm^{-1}. The ^1H NMR spectra contained resonances for the C_5H_5 protons at δ 4.49 and 4.72 ppm, respectively, and for the Me group in **3d** at δ 2.06 ppm. The molecular structure determination of **3g** completed the series of complexes containing ligands formed from dcfe and the (phenylethynyl)ruthenium moiety.

Molecular Structures of 1g, 2g, 2h, and 3g.

(a) $Ru[\overline{C{=}CPhC(CF_3)_2C}(CN)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$ (1g). A plot of a molecule of **1g** is shown in Figure 1, which also indicates the atom-numbering scheme. Coordination about ruthenium is distorted octahedral, with three facial sites being occupied by the C_5H_5 ligand (Ru-C = 2.247 (8)-2.273 (7) Å; average 2.258 Å); the other three positions have CO (Ru-CO = 1.843 (9) Å), PPh_3 (Ru-P = 2.309 (2) Å), and the σ-cyclobutenyl ligand (Ru-C(6) = 2.054 (8) Å). The molecule is chiral at Ru, and as the unit cell contains only one enantiomer, the compound has spontaneously resolved during the crystallization procedure.

Within the cyclobutenyl ring, the double bond C(6)-C(7) (1.35 (1) Å) and single bond C(7)-C(8) (1.53 (1) Å) fall within the normal limits of such bond distances. The two C-C bonds, opposite the double bond (C(8)-C(9) = 1.57 (1) Å) and from the metal-bonded carbon (C(6)-C(9) = 1.58 (1) Å), show a degree of lengthening that is now becoming familiar in these metal-bonded four-membered rings.[2] Table I summarizes some relevant data for all four ruthenium complexes described in this paper. Lengthening of the C(8)-C(9) bond is consistent with the isomerization process giving the butadienyls, but the long C-C bond adjacent to the metal may reflect some separation of charge, not fully shared on ring closure of the proposed zwitterionic intermediate.

The four-membered ring is essentially planar, with deviations from the least-squares plane through C(6)C(7)C(8)C(9) being <0.02 (1) Å. Angles within the C_4 ring are 91.0, 97.3 (6)° (at C(sp^2)) and 84.8, 86.8 (6)° (at C(sp^3)).

As found earlier,[2] addition of dcfe to the C≡C triple bond occurs in a preferred direction so that the $C(CN)_2$ group becomes attached to the α-carbon of the acetylide. No evidence for the formation of any isomeric addition product was obtained.

Table I. Selected Bond Lengths (Å) and Angles (deg) for Complexes 1g, 2g, 2h, and 3g

	compd			
param	**1g**	**2g**	**2h**	**3g**
Ru-P(1)	2.309 (2)	2.332 (1)	2.347 (1)	2.411 (2)
Ru-C(6)	2.054 (8)	2.100 (5)	2.106 (5)	1.977 (7)[a]
C(6)-C(7)	1.35 (1)	1.480 (7)	1.493 (8)	1.42 (1)
C(6)-C(9)	1.58 (1)	1.367 (7)	1.362 (8)	1.37 (1)
C(7)-C(8)	1.53 (1)	1.356 (7)	1.328 (8)	1.46 (1)
C(8)-C(9)	1.57 (1)			
Ru-C(6)-C(7)	140.9 (6)	120.0 (3)	116.7 (4)	76.0 (5)
Ru-C(6)-C(9)	126.1 (6)	123.9 (3)	128.3 (4)	149.9 (6)[b]
C(7)-C(6)-C(9)	91.0 (6)	113.5 (4)	113.2 (5)	131.4 (7)
C(6)-C(7)-C(8)	97.3 (6)	125.1 (4)	126.5 (5)	113.5 (6)
C(7)-C(8)-C(9)	84.8 (6)			
C(8)-C(9)-C(6)	86.8 (6)			

[a] Ru-C(7) = 2.138 (7) Å; Ru-C(8) = 2.202 (7) Å. [b] Ru-C(7)-C(6) = 63.8 (4)°; Ru-C(7)-C(8) = 72.7 (4)°; Ru-C(8)-C(7) = 68.0 (4)°.

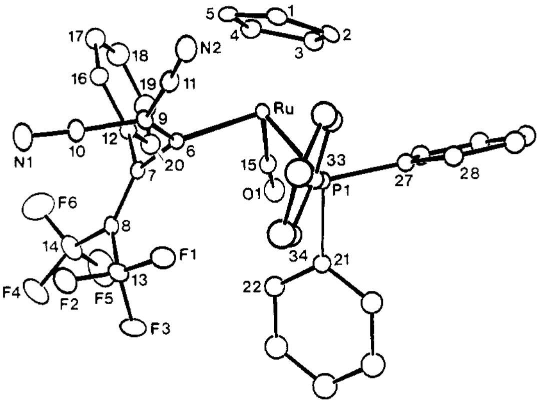

Figure 2. ORTEP view of $Ru[C({=}C(CN)_2)CPh{=}C(CF_3)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$ (**2g**) showing the atom-labeling scheme. Atoms not otherwise indicated are carbons.

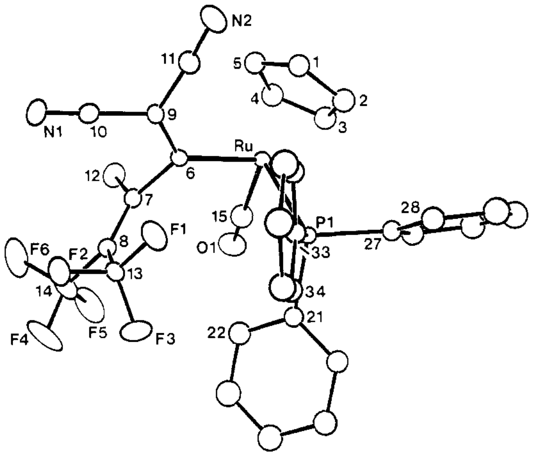

Figure 3. ORTEP view of $Ru[C({=}C(CN)_2)CMe{=}C(CF_3)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$ (**2h**) showing the atom-labeling scheme. Atoms not otherwise indicated are carbons.

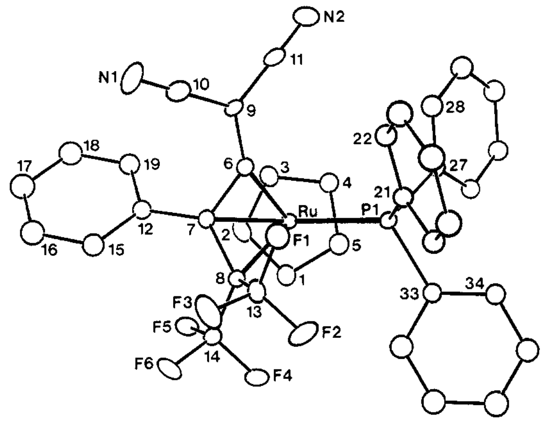

Figure 4. ORTEP view of Ru[η^3-C(CF_3)$_2$CPhC=C(CN)$_2$](PPh_3)(η-C_5H_5) (**3g**) showing the atom-labeling scheme. Atoms not otherwise indicated are carbons.

(b) Ru[C(=C(CN)$_2$)CX=C(CF_3)$_2$](CO)(PPh_3)(η-C_5H_5) (X = Ph (2g), Me (2h)). Plots of a molecule of each of these complexes are shown in Figures 2 and 3, and relevant interatomic parameters are listed in Table I. As with **1g**, the molecules are chiral at ruthenium, but in these cases each unit cell contains both enantiomers in equal amount. For ease of comparison, the same isomers have been illustrated. The coordination about the ruthenium is again distorted octahedral, the η-C_5H_5 group being somewhat asymmetrically attached to the metal (Ru–C(cp) 2.235–2.283 (6) Å, average 2.256 Å (**2g**); 2.217–2.269 (4) Å, average 2.244 Å (**2h**)), and the other three positions are occupied by CO (Ru–C(15) = 1.852 (16) Å (**2g**), 1.854 (6) Å (**2h**)), PPh_3 (Ru–P(1) = 2.332 (1) Å (**2g**), 2.347 (1) Å (**2h**)), and the substituted buta-1,3-dien-2-yl group (Ru–C(6) = 2.100 (5) Å (**2g**), 2.106 (5) Å (**2h**)). The slight asymmetry found in the Ru–C(cp) bond distances for **2g** and **2h** can be traced to the steric interaction between the =C(CN)$_2$ group of the organic ligand and the cyclopentadienyl ring. In order to minimize this interaction, the cyclopentadienyl ring is shifted slightly from the ideal octahedral face.

The butadienyl ligand is nonplanar (torsion angles C(8)C(7)C(6)C(9) = 73.1° (**2g**), 81.0° (**2h**)), and as a result, the C—C single and C=C double bonds are localized (C(6)–C(7) = 1.480 (7) Å (**2g**), 1.493 (8) Å (**2h**); C(6)–C(9), C(7)–C(8) = 1.367, 1.356 (7) Å (**2g**), 1.362, 1.328 (8) Å (**2h**)). This structural feature has been found previously[5] and arises because the bulk of the substituents on C(8) and C(9) precludes the adoption of a planar C_4 skeleton. There is no significant difference between the two ligands in **2h** and **2g** resulting from replacement of Me in the former by Ph in the latter.

(c) Ru[η^3-C(CF_3)$_2$CPhC=C(CN)$_2$](PPh_3)(η-C_5H_5) (3g). Figure 4 is a plot of a molecule of **3g**, with an atom-numbering scheme that is related as far as possible to those of the σ-bonded complexes in Figures 1–3; selected parameters are given in Table I. In **3g**, the metal is coordinated by the η-C_5H_5 group (Ru–C(cp) = 2.218–2.273 (8) Å, average 2.236 Å), a PPh_3 ligand (Ru–P(1) = 2.411 (2) Å), and the allylic ligand (Ru–C(6) = 1.977 (7) Å, Ru–C(7) = 2.138 (7) Å, Ru–C(8) = 2.202 (7) Å) formed by chelation of the butadienyl ligand via the C(7)–C(8) double bond with loss of CO.

The mode of attachment of the C_3 ligand, one terminal carbon of which is involved in an *exo*-allylic double bond, is interesting. In addition to complexes such as [Fe(CO)$_3$(η^3-C(CO_2Me)$_2$CHC=O)]$^-$, whose structure was inferred from spectroscopic data,[6] several other examples have been characterized by X-ray analyses, including Mo[OC(O)C_3F_7](CO)$_2$(bpy)[η^3-CH_2C(CONHMe)C=CH_2][7] and ML_n[η^3-C(CN)$_2$CPhC=C(CN)$_2$] (ML_n = W(CO)$_2$(η-C_5H_5),[8] Ru(PPh_3)(η-C_5H_5)[9]). These ligands are distinguished from classical η^3-allylic ligands by their pattern of M–C and C–C bond lengths. The M—C bond lengths divide into two longer bonds, consistent with an M—(η^2-C=C) interaction, and a short M—C separation involving C(6), indicating a degree of multiple-bond character for this bond. In addition, the two C–C bonds in the C_3 unit are similar; that for C(7)–C(8) (1.46 (1) Å) is consistent with a strong olefin–metal interaction, while C(6)–C(7) (1.42 (1) Å) is considerably shorter than expected for a C–C single bond.

Discussion

The reactions of dcfe with ruthenium acetylide complexes (Scheme I) occur by initial [2 + 2] cycloaddition to give the cyclobutenyls 1. Unlike the case for tetracyanoethene, there is no detectable paramagnetic, deep-colored intermediate; reactions are complete after several minutes, and the cyclobutenyls can be isolated without difficulty. Complexes 1 are formed as single isomers, in which the CF_3-bearing carbon of dcfe has added to the β-carbon of the ruthenium acetylide, and cyclization occurs by bond formation between the α-carbon and the dicyanomethylene moiety. These results are consistent with the theoretical predictions concerning the concentration of electron density on the β-carbon of transition-metal η^1-acetylides[26] and their consequent behavior as strong nucleophiles. In contrast with $C_2(CN)_4$, studied earlier, dcfe is a polarized dienophile; presumably the directed and selective cycloaddition found for this olefin results from the ability of the C(CN)$_2$ group to stabilize the negative charge in the proposed intermediate zwitterion.

This features may also account for the presence of a relatively long C–C bond involving the α-carbon of the original acetylide ligand, which is also observed in the related tungsten, manganese, and iron complexes[2] but not found in complexes derived from $C_2(CN)_4$. Internal angles at C(8) and C(9), only 85 and 87°, respectively, suggest an unusual degree of strain in this system. Again, withdrawal of negative charge onto the C(CN)$_2$ group may be the cause of these unusual structural features.

The other long C–C bond, between C(8) and C(9), is the one that is broken in the rearrangement of the cyclobutene to the butadiene, and the geometry predisposes this isomerization. The reaction is much slower than that found with complexes derived from $C_2(CN)_4$ and may be related to the "incomplete" cyclization indicated by the long C(6)–C(9) bond, referred to above. However, heating complexes 1 in refluxing toluene or xylene resulted in conversion to the corresponding butadienyls 2. These have been fully characterized on earlier occasions,[2,5] and the present examples also exhibit the characteristic nonplanar, localized 1,3-diene structure.

Similar structural features and ring-opening reactions have been described for the complex Fe[$\overline{\mathrm{C{=}CPhC}}$-

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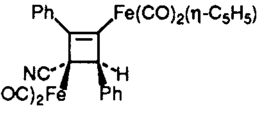
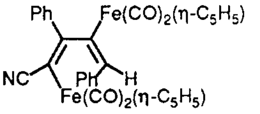
(CN)(Fe(CO)$_2$(η-C$_5$H$_5$))CHPh](CO)$_2$(η-C$_5$H$_5$) (4).[10] The



4

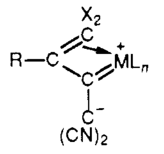
C–C bonds joining the carbons bearing the metal substituents (C(3)–C(4) = 1.57 (4) Å, C(4)–C(1) = 1.58 (4) Å) are long (although the esd's are high); the Fe–C(sp^2) bond (1.89 (3) Å) is slightly shorter than expected. The cyanobutadiene complex 5 formed by cleavage of the C(1)–C(4) bond also contains a nonplanar C$_4$ diene moiety (torsional angle about C(2)–C(3) 88.4°).



5

Further transformation of the ruthenium complexes into those containing the related η^3-allyl system has also been observed. Again, this transformation is less facile than found with C$_2$(CN)$_4$; we recall that the product isolated from the reaction between Ru(C$_2$Ph)(PPh$_3$)$_2$(η-C$_5$H$_5$) and the cyanoolefin was Ru(PPh$_3$)[η^3-C(CN)$_2$CPhC=C(CN)$_2$](η-C$_5$H$_5$), no intermediates, apart from the initial paramagnetic complex, being detected.[8,9] Structurally, these allylic systems contain a short M–C bond, suggesting a degree of double bonding; the ^{13}C chemical shift of the metal-bonded carbon (ca. 200 ppm) is also consistent with this observation. It is interesting that the bond multiplicity develops during the conversion of the butadienyl to the allyl ligand, i.e. upon chelation, the Ru–C(6) bonds in **1g**, **2g**, and **2h** being in the normal range of Ru–C(sp^2) separations. However, we note that the ^{13}C resonances of C(6) in the butadienyls are also found at relatively low field.

These results are consistent with the zwitterionic formulation A, in which the negative charge is stabilized by the dicyanomethylene fragment. Thus, these derivatives



A

join the growing number of complexes containing unsaturated ligands attached to second- and third-row transition metals, particularly those of groups 5–8, via M=C(sp^2) multiple bonds. Some examples include η^2(3e)-vinyl,[11-13] η^3(4e)-allylidene,[14] η^4(5e)-butadienyl,[15] and butenediyl[16,17] complexes; the last can also be viewed as containing metallacyclopentatriene systems, the degree of planarity of which depends critically on the d-electron count.[17,18] A related nitrogen-containing metallacycle has also been described.[19]

Experimental Section

General Conditions. All reactions were performed under nitrogen with use of dried, degassed solvents; no special precautions were taken to exclude air during workup since most complexes proved to be stable in air as solids and for short times in solution. Photochemical reactions were performed by using a Philips 100-W high-pressure Hg lamp with quartz immersion wells. Microanalyses were performed by the Canadian Microanalytical Service, Vancouver, British Columbia, Canada.

Instruments: Perkin-Elmer 683 double-beam spectrometer, NaCl optics (IR); Bruker CXP300 spectrometer (^{1}H NMR at 300.13 MHz, ^{13}C NMR at 75.47 MHz); Bruker WP80 spectrometer (^{1}H NMR at 80 MHz; ^{13}C NMR at 20.1 MHz). Chemical shifts to low field are denoted positive; the internal reference was TMS (^{13}C and ^{1}H NMR). FAB mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon or xenon was used as the exciting gas, with source pressures typically 10^{-6} mbar; the FAB gun voltage was 7.5 kV, with current 1 mA. The ion accelerating potential was 7 kV. The matrix was 3-nitrobenzyl alcohol. The complexes were made up as ca. 0.5 M solutions in CH$_2$Cl$_2$; a drop was added to a drop of matrix, and the mixture was applied to the FAB probe tip. Spectra are reported below in the following form: m/z, assignment, relative intensity. Multiisotopic species are normalized on the most abundant metal isotope (^{102}Ru). All metal-containing ions with relative intensity greater than 10% of the base peak are listed together with assigned minor ions. Peaks marked with an asterisk are the strongest of multiplets related to the assigned formulation by addition or loss of one or two H atoms.

Starting Materials. Literature methods were used to prepare Ru(C$_2$Ph)(CO)(PPh$_3$)(η-C$_5$H$_5$),[20] Ru(C$_2$Ph)(dppe)(η-C$_5$H$_5$),[20] Ru(C$_2$Ph)(PPh$_3$)$_2$(η-C$_5$H$_5$),[20] Ru(C$_2$Me)(PPh$_3$)$_2$(η-C$_5$H$_5$),[20] and C(CN)$_2$=C(CF$_3$)$_2$ (dcfe).[21]

Syntheses. (1) Preparation of Cyclobutenyl Complexes. (a) Ru[C=CMeC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)$_2$(η-C$_5$H$_5$) (1d). (i) To a suspension of Ru(C$_2$Me)(PPh$_3$)$_2$(η-C$_5$H$_5$) (200 mg, 0.27 mmol) in MeCN (35 mL) was added dcfe (74 mg, 0.35 mmol). The solid quickly went into solution, and after the mixture was stirred for 24 h, the resulting yellow precipitate was filtered off, washed with MeCN and petroleum spirit, and dried under vacuum. Low-temperature crystallization (petroleum spirit/CH$_2$Cl$_2$) gave yellow microcrystalline Ru[C=CMeC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)$_2$(η-C$_5$H$_5$)·0.25CH$_2$Cl$_2$ (**1d**; 210 mg, 0.22 mmol, 81%) mp 179–180 °C dec. Anal. Calcd for C$_{50}$H$_{38}$F$_6$N$_2$P$_2$Ru·0.25CH$_2$Cl$_2$: C, 62.84; H, 4.00; N, 2.90; M_r, 944 (unsolvated). Found: C, 62.84; H, 4.02; N, 2.93; M_r (mass spectrometry), 944.

(ii) Ru[C=CMeC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)$_2$(η-C$_5$H$_5$) was also prepared by the addition of dcfe (248 mg, 1.16 mmol) to a solution of Ru(C$_2$Me)(PPh$_3$)$_2$(η-C$_5$H$_5$) (700 mg, 0.96 mmol) in toluene (20 mL). After 30 h **1d** had precipitated as a yellow powder (743 mg, 82%), mp 161–163 °C. Anal. Calcd for C$_{50}$H$_{38}$F$_6$N$_2$P$_2$Ru: C, 63.6; H, 4.1; N, 3.0. Found: C, 62.8; H, 4.0; N, 3.0. IR (Nujol, cm^{-1}): ν(CN) 2238 vw; ν(CC) 1572 m; ν(CF) 1282 (sh), 1270 vs, 1255 (sh), 1236 (sh), 1220 s, 1197 vs, 1185 (sh); other peaks at 1488 s, 1311 w, 1158 w, 1140 m, 1112 w, 1087 s, 1078 (sh), 1036 w, 1014 w, 1000 m, 933 m, 873 m, 838 m, 825 (sh), 810 m, 752 s, 750 (sh), 747 (sh), 739 m, 713 (sh), 700 vs, 680 (sh). ^{1}H NMR (δ CDCl$_3$): 7.2–6.9 (m, 30 H, Ph), 4.64 (s, 5 H, η-C$_5$H$_5$), 0.53 (s, 3 H, Me). ^{13}C{^{1}H}

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Table II. Crystal and Intensity Collection Data for Complexes 1g, 2g, 2h, and 3g

	1g	**2g**	**2h**	**3g**
formula	$C_{38}H_{25}F_6N_2OPRu$	$C_{38}H_{25}F_6N_2OPRu$	$C_{33}H_{23}F_6N_2OPRu$	$C_{37}H_{25}F_6N_2PRu{\cdot}H_2O$
M_r	771.6	771.6	709.6	761.7
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_12_12_1$ (D_2^4, No. 19)	$P2_1/n$ (C_{2h}^5, No. 14)	$C2/c$ (C_{2h}^6, No. 15)	$P2_1$/n (C_{2h}^5, No. 14)
a, Å	10.409 (2)	14.942 (1)	22.237 (4)	13.804 (3)
b, Å	16.227 (3)	13.413 (2)	18.648 (5)	17.257 (2)
c, Å	20.000 (3)	16.928 (6)	17.731 (3)	13.957 (3)
β, deg	90	97.02 (1)	124.93 (2)	98.49 (2)
V, Å^3	3378.1	3367.2	6028.1	3288.3
Z	4	4	8	4
D_{calcd}, g cm^{-3}	1.517	1.522	1.564	1.539
$F(000)$	1552	1552	2848	1528
μ, cm^{-1}	5.31	5.33	5.91	5.45
θ range, deg	1–25	1–22.5	1.5–24	1–22.5
no of rflns measd	4334	5857	4288	4924
no. of unique rflns	4064	4405	4288	4242
no. of unique rflns used with $I \geq 2.5\sigma(I)$	2851	3659	3076	2922
R	0.040	0.045	0.039	0.055
k	1.0	0.3	3.0	1.0
g	0.0013	0.0060	0.0001	0.0048
R_w	0.041	0.059	0.042	0.062
ρ_{max}, e Å^{-3}	0.62	0.99	0.80	1.52

NMR (δ, $CDCl_3$): 149.6 (t, J(CP) = 4 Hz, RuC), 140.4–127.7 (m, Ph), 116.4 (s, CN), 84.8 (s, η-C_5H_5), 16.4 (s, Me), other resonances were not observed. FAB MS: 944, $[M]^+$, 25; 867, $[M - Ph]^+$, 3; 691*, $[Ru(PPh_3)_2(C_5H_5)]^+$, 7; 682*, $[M - PPh_3]^+$, 55; 625*, $[Ru(PPh_3)_2]^+$, 6; 613*, $[691 - Ph]^+$, 6; 427*, $[Ru(PPh_3)(C_5H_5)]^+$, 100; 363*, $[Ru(PPh_3)]^+$, 13; 350*, $[Ru(PPh_2)(C_5H_5)]^+$, 20; 224*, $[RuPh(C_5H_5)]^+$, 19.

(b) $\mathbf{Ru[\overline{C{=}CPhC(CF_3)_2C}(CN)_2](PPh_3)_2(\eta\text{-}C_5H_5)}$ (1e). The olefin (76 mg, 0.36 mmol) was added to a suspension of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.25 mmol) in MeCN (50 mL). After 1 min all the solid had dissolved and the reaction mixture was cooled to 0 °C. The resulting precipitate was collected after 5 min, washed with MeCN and petroleum spirit, and dried under vacuum, giving a yellow powder of $Ru[\overline{C{=}CPhC(CF_3)_2C}(CN)_2](PPh_3)_2(\eta\text{-}C_5H_5)$ (**1e**; 192 mg, 0.19 mmol, 76%), mp 145–146 °C dec. Anal. Calcd for $C_{55}H_{40}F_6N_2P_2Ru$: C, 65.67; H, 4.01; N, 2.78; M_r, 1006. Found: C, 65.36; H, 4.02; N, 3.05; M_r (mass spectrometry), 1006. Infrared (Nujol, cm^{-1}): ν(CN) 2239 vw; ν(CC) 1587 w, 1572 vw; ν(CF) 1287 (sh), 1269 vs, 1219 m, 1199 vs; other peaks at 1520 w, 1435 s, 1244 wm, 1238 w, 1160 w, 1138 w, 1115 (sh), 1106 m, 1088 m, 1077 (sh), 1063 w, 1027 w, 1002 w, 947 m, 848 w, 831 m, 817 m, 754 m, 745 m, 740 m, 720 m, 704 s, 698 s, 681 w. FAB MS: 1006, $[M]^+$, 14; 929, $[M - Ph]^+$, 1; 792, $[M - dcfe]^+$, 11; 744, $[M - PPh_3]^+$, 34; 691, $[Ru(PPh_3)_2(C_5H_5)]^+$, 38; 530, $[M - dcfe - PPh_3]^+$, 7; 453*, $[M - dcfe - PPh_3 - Ph]^+$, 10; 444, $[M - dcfe - PPh_3 - Ph + O]^+$, 9; 429, $[Ru(PPh_3)(C_5H_5)]^+$, 100; 350*, $[Ru(PPh_2)(C_5H_5)]^+$, 21; 244, $[RuPh(C_5H_5)]^+$, 19. As this complex is unstable in solution, no NMR data could be obtained.

(c) $\mathbf{Ru[\overline{C{=}CPhC(CF_3)_2C}(CN)_2](dppe)(\eta\text{-}C_5H_5)}$ (1f). A mixture of $Ru(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$ (100 mg, 0.15 mmol) and dcfe (60 mg, 0.28 mmol) in benzene (10 mL) was stirred for 24 h. To the filtered solution was added octane (5 mL), and the volume was then reduced to 5 mL. The resulting pale yellow precipitate was washed with petroleum spirit and dried under vacuum. Crystallization (benzene/petroleum spirit) gave yellow microcrystalline $Ru[\overline{C{=}CPhC(CF_3)_2C}(CN)_2](dppe)(\eta\text{-}C_5H_5)$ (**1f**; 105 mg, 0.12 mmol, 80%), mp 230–231 °C. Anal. Calcd for $C_{45}H_{34}F_6N_2P_2Ru$: C, 61.43; H, 3.89; N, 3.18; M_r, 880. Found: C, 61.63; H, 4.00; N, 3.14; M_r (mass spectrometry), 880. Infrared (Nujol, cm^{-1}): ν(CN) 2233 vw; ν(CC) 1606 w, 1586 w, 1573 w; ν(CF) 1292 (sh), 1274 s, 1250 (sh), 1230 s, 1220 (sh), 1208 s, 1199 s, 1165 s, 1110 s; other bands at 1546 w, 1310 (sh), 1105 (sh), 1077 w, 1068 w, 1030 w, 1002 w, 969 m, 942 m, 910 w, 855 w, 817 m, 788 w, 770 w, 751 m, 739 m, 722 s, 708 (sh), 700 s, 675 s, 630 w. ^1H NMR (δ, $CDCl_3$): 8.0–6.6 (m, 20 H, PPh), 6.72 (t, J(HH) = 7 Hz, 3 H, Ph), 5.27 (d, J(HH) = 8 Hz, 2 H, Ph), 4.71 (s, 5 H, C_5H_5), 2.52 (m, 4 H, CH_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 178.6 (m, C_α), 147.2–128.4 (m, Ph), 115.6 (m, CN), 85.4 (s, C_5H_5), 29.2 (t, J(CP) = 22 Hz, CH_2); other minor peaks at 71.6 (s), 70.0 (s), 58.7 (s), 8.4 (s). FAB MS: 888, $[M]^+$, 61; 803, $[M - Ph]^+$, 14; 734, $[M - Ph - CF_3]^+$, 5; 666, $[M - dcfe]^+$, 91; 601*, $[M - dcfe - C_5H_5]^+$, 7; 589*, $[M - dcfe - Ph]^+$, 7; 581*, $[565 + O]^+$, 5; 565, $[Ru(dppe)(C_5H_5)]^+$, 100; 499*, $[Ru(dppe)]^+$, 12; 459*, $[Ru(P_2Ph_3)(C_5H_5)]^+$, 13; 393*, $[RuP_2Ph_3]^+$, 13; 378*, $[RuC_2(PPh_2)(C_5H_5)]^+$, 26; 363*, $[Ru(PPh_3)]^+$, 12; 351*, $[Ru(PPh_2)(C_5H_5)]^+$, 47; 317*, $[RuP_2Ph_2]^+$, 17; 299*, $[RuC_2(PPh)(C_5H_5)]^+$, 14; 244*, $[RuPh(C_5H_5)]^+$, 14, 167, $[Ru(C_5H_5)]^+$, 13.

(d) $\mathbf{Ru[\overline{C{=}CPhC(CF_3)_2C}(CN)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)}$ (1g). (i) A mixture of dcfe (80 mg, 0.37 mmol) and $Ru(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (100 mg, 0.18 mmol) in benzene (10 mL) was stirred for 20 h. The volume was reduced to 5 mL, and n-octane (5 mL) was added; further volume reduction resulted in a white precipitate. This was collected, washed with petroleum spirit, dried under vacuum, and crystallized (petroleum spirit/CH_2Cl_2), yielding colorless crystals of $Ru[\overline{C{=}CPhC(CF_3)_2C}(CN)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$ (**1g**; 117 mg, 0.15 mmol, 84%), mp 206–207 °C. Anal. Calcd for $C_{38}H_{25}F_6N_2OPRu$: C, 59.15; H, 3.27; N, 3.63; M_r, 772. Found: C, 59.13; H, 3.27; N, 3.65; M_r (mass spectrometry), 772. Infrared (CH_2Cl_2, cm^{-1}): ν(CN) 2240 vw; ν(CO) 1960 s. Infrared (Nujol, cm^{-1}): ν(CN) 2247 vw; ν(CO) 1980 (sh), 1954 vs, 1918 w; ν(CC) 1611 w, 1572 w; ν(CF) 1295 (sh), 1278 s, 1250 (sh), 1222 m, 1210 s; other peaks at 1487 m, 1150 w, 1114 w, 1100 m, 1095 m, 1077 w, 1065 w, 1030 w, 1002 w, 948 m, 900 w, 840 m, 821 s, 760 m, 748 w, 722 m, 708 m, 697 s, 680 w, 638 w. ^1H NMR (δ, $CDCl_3$): 7.4–7.2 (m, 15 H, PPh), 7.0–6.8 (m, 5 H, Ph), 5.02 (s, 5 H, C_5H_5). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 219.6 (s, (br), CO), 172.7 (d, J(CP) = 35 Hz, C_α), 136.2–126.7 (m, Ph), 114.8 (d, J = 11 Hz, CN), 113.4 (d, J = 8 Hz, CN), 87.3 (s, C_5H_5); other minor peaks at 154 (s), 42.5 (s), 35.3 (s). FAB MS: 772, $[M]^+$, 84; 744*, $[M - CO]^+$, 15; 667, $[M - CO - Ph]^+$, 15; 558, $[M - dcfe]^+$, 11; 529*, $[M - dcfe - CO]^+$, 7; 482, $[M - PPh_3 - CO]^+$, 12; 456*, $[M - PPh_3 - CO - CN]^+$, 20; 453*, $[M - dcfe - Ph - CO]^+$, 28; 429*, $[Ru(PPh_3)(C_5H_5)]^+$, 100; 363*, $[Ru(PPh_3)]^+$, 22; 350*, $[Ru(PPh_2)(C_5H_5)]^+$, 32; 285*, $[Ru(PPh_2)]^+$, 18; 224, $[RuPh(C_5H_5)]^+$, 23; 167*, $[Ru(C_5H_5)]^+$, 24.

(ii) $Ru(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (15 mg, 0.027 mmol) dissolved in benzene-d_6 (0.5 mL) was added to dcfe (6 mg, 0.03 mmol) and then placed in an NMR tube. After 3 min the formation of the cyclobutenyl complex **1g** was complete.

(iii) A solution of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (290 mg, 0.37 mmol) in benzene (50 mL) was saturated with CO, and dcfe (167 mg, 0.78 mmol) was added. The reaction mixture was left under positive CO pressure for 5 days. Following this the volume was reduced (to 10 mL) and n-octane (10 mL) was added; further evaporation resulted in precipitation of an off-white solid, which was purified by TLC to give $Ru[\overline{C{=}CPhC(CF_3)_2C}(CN)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$ (**1g**; 180 mg, 0.23 mmol, 63%), identified by FAB MS, ^1H NMR, and infrared spectra.

Table III. Fractional Atomic Coordinates (×10^5 for Ru; ×10^4 for Other Atoms) for $Ru[\overline{C{=}CPhC(CF_3)_2C}(CN)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$ (1g)

atom	*x*	*y*	*z*
Ru	−1908 (6)	33256 (3)	22467 (3)
P(1)	252 (2)	3773 (1)	3318 (1)
F(1)	4157 (6)	4831 (3)	1841 (3)
F(2)	5523 (6)	4000 (4)	1430 (4)
F(3)	4463 (7)	4804 (3)	781 (3)
F(4)	4755 (9)	2646 (4)	907 (3)
F(5)	3862 (8)	3381 (4)	130 (3)
F(6)	2797 (8)	2477 (3)	664 (3)
O(1)	−1256 (8)	4981 (4)	1855 (4)
N(1)	427 (11)	3553 (5)	236 (4)
N(2)	1684 (10)	5627 (5)	1264 (4)
C(1)	−209 (11)	1948 (4)	2385 (4)
C(2)	−1407 (10)	2281 (5)	2626 (5)
C(3)	−2065 (10)	2658 (6)	2086 (5)
C(4)	−1302 (11)	2558 (6)	1500 (5)
C(5)	−164 (11)	2113 (5)	1678 (5)
C(6)	1605 (8)	3568 (4)	1868 (4)
C(7)	2832 (7)	3308 (5)	1915 (3)
C(8)	3311 (8)	3679 (5)	1258 (4)
C(9)	1909 (9)	4029 (5)	1194 (3)
C(10)	1124 (11)	3750 (5)	635 (4)
C(11)	1787 (9)	4942 (6)	1228 (4)
C(12)	3549 (5)	2799 (3)	2397 (3)
C(13)	4377 (11)	4324 (6)	1318 (5)
C(14)	3702 (13)	3041 (6)	733 (5)
C(15)	−785 (9)	4357 (5)	2016 (4)
C(16)	4365 (5)	3160 (3)	2866 (3)
C(17)	5053 (5)	2666 (3)	3311 (3)
C(18)	4924 (5)	1811 (3)	3286 (3)
C(19)	4108 (5)	1450 (3)	2817 (3)
C(20)	3421 (5)	1944 (3)	2372 (:3)
C(21)	1665 (5)	4406 (3)	3487 (2)
C(22)	1942 (5)	5032 (3)	3032 (2)
C(23)	2907 (5)	5603 (3)	3174 (2)
C(24)	3594 (5)	5547 (3)	3771 (2)
C(25)	3317 (5)	4920 (3)	4226 (2)
C(26)	2353 (5)	4349 (3)	4084 (2)
C(27)	391 (5)	2939 (3)	3927 (2)
C(28)	1422 (5)	2396 (3)	3862 (2)
C(29)	1555 (5)	1738 (3)	4305 (2)
C(30)	657 (5)	1623 (3)	4814 (2)
C(31)	−374 (5)	2166 (3)	4880 (2)
C(32)	−507 (5)	2824 (3)	4436 (2)
C(33)	−1020 (5)	4430 (3)	3677 (2)
C(34)	−2269 (5)	4355 (3)	3432 (2)
C(35)	−3254 (5)	4833 (3)	3703 (2)
C(36)	−2990 (5)	5385 (3)	4220 (2)
C(37)	−1741 (5)	5460 (3)	4465 (2)
C(38)	−756 (5)	4982 (3)	4194 (2)

(2) Thermal Isomerization of Cyclobutenes to Butadienes. (a) $Ru[C(=C(CN)_2)CPh=C(CF_3)_2](dppe)(\eta\text{-}C_5H_5)$ (2f). A solution of $Ru[\overline{C{=}CPhC(CF_3)_2C}(CN)_2](dppe)(\eta\text{-}C_5H_5)$ (50 mg, 0.057 mmol) in xylene (20 mL) was refluxed for 5 h and cooled and the solvent removed under reduced pressure. The residue was purified by TLC (petroleum spirit/EtOH/Et$_2$O, 4:1:1) to give a major yellow band (R_f 0.18), which was collected and crystallized (CH$_2$Cl$_2$/petroleum spirit), giving yellow crystalline $Ru[C(=C(CN)_2)CPh=C(CF_3)_2](dppe)(\eta\text{-}C_5H_5)\cdot 0.25CH_2Cl_2$ (**2f**; 15 mg, 0.017 mmol, 30%), mp 223–224 °C. Anal. Calcd for $C_{45}H_{34}F_6N_2P_2Ru\cdot 0.25CH_2Cl_2$: C, 60.32; H, 3.86; N, 3.11; M_r, 880 (unsolvated). Found: C, 60.54; H, 3.90; N, 3.12; M_r (mass spectrometry), 880. Infrared (Nujol, cm^{-1}): ν(CN) 2205 m, 2190 m; ν(CC) 1590 m, 1570 m; ν(CF) 1243 s, 1218 s, 1199 s, 1140 s; other peaks at 1489 w, 1438 s, 1427 s, 1329 s, 1319 s, 1092 w, 1046 m, 1029 w, 1000 w, 952 m, 872 w, 850 m, 840 m, 819 m, 772 w, 750 m, 723 m, 697 s, 627 m, 645 w. ^{1}H NMR (δ, CDCl$_3$): 7.4–7.2 (m, 25 H, Ph), 5.30 (s, 0.5 H, CH$_2$Cl$_2$), 4.67 (s, 1 H, C$_5$H$_5$), 4.30 (s, 4 H, C$_5$H$_5$), 3.5–2.5 (m, 4 H, CH$_2$). FAB MS: 880, [M]$^+$, 38; 803, [M − Ph]$^+$, 8; 565, [Ru(dppe)(C$_5$H$_5$)]$^+$, 100; 499*, [Ru(dppe)]$^+$, 6; 378*, [Ru(PPh$_2$C$_2$)(C$_5$H$_5$)]$^+$, 13; 349*, [Ru(PPh$_2$)(C$_5$H$_5$)]$^+$, 21; 317*, [RuP$_2$Ph$_2$]$^+$, 8; 299*, [Ru(PPhC$_2$)(C$_5$H$_5$)]$^+$, 8; 244*, [RuPh(C$_5$H$_5$)]$^+$, 9; 167, [Ru(C$_5$H$_5$)]$^+$, 5.

Table IV. Fractional Atomic Coordinates (×10^5 for Ru; ×10^4 for Other Atoms) for $Ru[C(=C(CN)_2)CPh=C(CF_3)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$ (2g)

atom	*x*	*y*	*z*
Ru	52481 (2)	24004 (3)	15225 (2)
P(1)	3847 (1)	1903 (1)	1856 (1)
F(1)	4025 (2)	4449 (3)	2868 (2)
F(2)	4405 (3)	5890 (3)	3296 (3)
F(3)	4531 (3)	4640 (3)	4090 (2)
F(4)	5954 (3)	5881 (4)	4242 (3)
F(5)	6633 (5)	4492 (4)	4324 (3)
F(6)	6973 (3)	5612 (4)	3524 (3)
O(1)	6154 (3)	1594 (3)	3064 (3)
N(1)	5062 (4)	6522 (4)	1660 (3)
N(2)	3761 (4)	4461 (4)	60 (3)
C(1)	5039 (5)	2424 (4)	164 (4)
C(2)	5121 (4)	1417 (4)	437 (3)
C(3)	5973 (4)	1273 (4)	864 (3)
C(4)	6473 (4)	2188 (5)	876 (4)
C(5)	5876 (4)	2884 (5)	443 (3)
C(6)	5197 (3)	3904 (3)	1858 (3)
C(7)	5833 (3)	4287 (3)	2529 (3)
C(8)	5591 (4)	4756 (4)	3181 (3)
C(9)	4799 (3)	4639 (3)	1377 (3)
C(10)	4939 (4)	5691 (4)	1551 (3)
C(11)	4230 (4)	4496 (4)	651 (3)
C(12)	6796 (3)	4147 (3)	2402 (2)
C(13)	4641 (4)	4939 (5)	3353 (4)
C(14)	6289 (5)	5185 (6)	3813 (4)
C(15)	5781 (4)	1956 (4)	2504 (3)
C(16)	7094 (3)	4620 (3)	1748 (2)
C(17)	7964 (3)	4444 (3)	1561 (2)
C(18)	8536 (3)	3795 (3)	2029 (2)
C(19)	8237 (3)	3323 (3)	2682 (2)
C(20)	7367 (3)	3499 (3)	2869 (2)
C(21)	3654 (2)	1845 (3)	2901 (2)
C(22)	4223 (2)	2341 (3)	3488 (2)
C(23)	4087 (2)	2252 (3)	4286 (2)
C(24)	3381 (2)	1668 (3)	4496 (2)
C(25)	2811 (2)	1173 (3)	3910 (2)
C(26)	2948 (2)	1262 (3)	3112 (2)
C(27)	3651 (2)	588 (2)	1579 (2)
C(28)	2854 (2)	244 (2)	1151 (2)
C(29)	2758 (2)	−765 (2)	959 (2)
C(30)	3458 (2)	−1429 (2)	1194 (2)
C(31)	4255 (2)	−1085 (2)	1622 (2)
C(32)	4352 (2)	−76 (2)	1815 (2)
C(33)	2860 (3)	2560 (3)	1359 (2)
C(34)	2306 (3)	3129 (3)	1789 (2)
C(35)	1567 (3)	3634 (3)	1393 (2)
C(36)	1383 (3)	3571 (3)	567 (2)
C(37)	1937 (3)	3002 (3)	136 (2)
C(38)	2676 (3)	2497 (3)	532 (2)

(b) $Ru[C(=C(CN)_2)CPh=C(CF_3)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$ (2g). A solution of $Ru[\overline{C{=}CPhC(CF_3)_2C}(CN)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$ (100 mg, 0.13 mmol) in xylene (30 mL) was refluxed vigorously for 2 days. After the solution was cooled, the solvent was removed under reduced pressure and the residue chromatographed (TLC; petroleum spirit/acetone/CH$_2$Cl$_2$, 4:1:1). The major yellow band (R_f 0.46) was crystallized (petroleum spirit/CH$_2$Cl$_2$) to give yellow crystals of $Ru[C(=C(CN)_2)CPh=C(CF_3)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$ (**2g**; 20 mg, 0.026 mmol, 20%), mp 250–251 °C dec. Anal. Calcd for $C_{38}H_{25}F_6N_2OPRu$: C, 59.15; H, 3.27; N, 3.63; M_r, 772. Found: C, 59.06; H, 3.29; N, 3.65; M_r (mass spectrometry), 772. Infrared (CH$_2$Cl$_2$, cm^{-1}): ν(CN) 2210 m, 2205 m; ν(CO) 1974 s, 1957 (sh). Infrared (Nujol, cm^{-1}): ν(CN) 2215 m; ν(CO) 1955 vs, 1910 w; ν(CC) 1609 m, 1597 w, 1577 w; ν(CF) 1245 s, 1217 m, 1206 s, 1152 vs; other peaks at 1482 m, 1436 m, 1329 m, 1318 m, 1130 m, 1110 (sh), 1098 (sh), 1090 m, 1072 (sh), 1061 (sh), 1057 m, 1019 w, 1000 m, 961 s, 864 m, 802 w, 840 s, 829 (sh), 820 s, 777 m, 754 s, 750 (sh), 738 s, 729 w, 712 (sh), 702 s, 691 s, 682 (sh), 647 m, 636 m. ^{1}H NMR (δ, CDCl$_3$): 7.4–7.2 (m, 20 H, Ph), 4.61 (s, 5 H, C$_5$H$_5$). FAB MS: 772, [M]$^+$, 14; 744, [M − CO]$^+$, 11; 667, [M − CO − Ph]$^+$, 4; 482, [M − PPh$_3$ − CO]$^+$, 10; 456, [M − PPh$_3$ − CO − CN]$^+$, 37; 453*, [M − dcfe − Ph − CO]$^+$, 28; 429, [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$, 100; 363*, [Ru(PPh$_3$)]$^+$, 11; 350*, [Ru(PPh$_2$)(C$_5$H$_5$)]$^+$, 16; 244, [RuPh(C$_5$H$_5$)]$^+$, 10; 167, [(C$_5$H$_5$)Ru]$^+$,

12. Other minor/trace bands (eight) were observed but not characterized.

(3) Photolytic Conversion of a Butadienyl to an Allyl Complex. $Ru[\eta^3\text{-}C(CF_3)_2CPhC{=}C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)$ (3g). A solution of $Ru[C({=}C(CN)_2)CPh{=}C(CF_3)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$ (30 mg, 0.039 mmol) in dme (15 mL) was irradiated for 24 h at 24 °C. The solvent was then removed and the residue chromatographed (TLC; petroleum spirit/acetone/CH_2Cl_2, 3:1:1). Of the eight bands observed, only an orange band (R_f 0.67) was isolated. This crystallized (petroleum spirit/CH_2Cl_2) as orange crystalline $Ru[\eta^3\text{-}C(CF_3)_2CPhC{=}C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)\cdot 0.5CH_2Cl_2\cdot H_2O$ (**3g**; 7 mg, 0.009 mmol, 23%), mp 211–212 °C. Anal. Calcd for $C_{37}H_{25}F_6N_2PRu\cdot 0.5CH_2Cl_2\cdot H_2O$: C, 56.01; H, 3.25; N, 3.48; M_r, 744 (unsolvated). Found: C, 55.92; H, 3.28; N, 3.52; M_r (mass spectrometry), 744. Infrared (Nujol, cm^{-1}): ν(CN) 2220 s, 2217 (sh); ν(CC) 1567 vs; ν(CF) 1291 s, 1279 m, 1243 s, 1195 vs, 1182 (sh), 1161 m, 1130 vs, 1092 s; other peaks at 2060 w, 1499 (sh), 1492 (sh), 1484 m, 1450 m, 1442 s, 1417 m, 1347 s, 1320 w, 1308 m, 1221 w, 1087 (sh), 1075 (sh), 1033 m, 1000 w, 954 s, 886 m, 857 m, 842 s, 820 m, 805 s, 777 m, 764 (sh), 752 s, 740 s, 727 w, 711 (sh), 702 s, 690 m, 669 (sh), 640 w, 629 w. ^{1}H NMR (δ, $CDCl_3$): 8.0–7.3 (m, 20 H, Ph), 5.29 (s, 1 H, CH_2Cl_2), 4.72 (s, 5 H, C_5H_5) (complexed water under residual water peak in $CDCl_3$). FAB MS: 744, [M]$^+$, 40; 456*, $[Ru(CN)(PPh_3)(C_5H_5)]^+$, 21; 429*, $[Ru(PPh_3)(C_5H_5)]^+$, 100; 350 *, $[Ru(PPh_2)(C_5H_5)]^+$, 13.

(4) Thermal Conversion of a Cyclobutenyl to an Allyl Complex. $Ru[\eta^3\text{-}C(CF_3)_2CMeC{=}C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)$ (3d). A suspension of $Ru[C{=}CMeC(CF_3)_2C(CN)_2](PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.21 mmol) in MeCN (30 mL) was refluxed for 4 h and then cooled to room temperature. Unreacted starting material was then filtered off and the solvent removed under reduced pressure. The residue was chromatographed (Florisil column) with petroleum spirit as the eluent to remove PPh_3. A yellow band removed with CH_2Cl_2 was crystallized (petroleum spirit/CH_2Cl_2) to give yellow crystalline $Ru[\eta^3\text{-}C(CF_3)_2CMeC{=}C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)\cdot 0.5CH_2Cl_2$ (**3d**; 100 mg, 0.14 mmol, 66%), mp 192–194 °C. Anal. Calcd for $C_{32}H_{23}F_6N_2PRu\cdot 0.5CH_2Cl_2$: C, 53.84; H, 3.33; N, 3.86; M_r (unsolvated), 682. Found: C, 53.64; H, 3.33; N, 3.83; M_r (mass spectrometry), 682. Infrared (Nujol, cm^{-1}): ν(CN) 2222 s; ν(CC) 1587 s; ν(CF) 1303 s, 1276 m, 1240 s, 1230 s, 1207 (sh), 1201 s, 1188 m, 1167 m, 1144 s, 1122 s, 1095 s, 1086 s; other peaks at 1482 m, 1442 s, 1417 m, 1368 s, 1358 s, 1314 m, 1060 m, 1029 s, 1022 s, 1002 w, 992 w, 967 s, 933 s, 850 m, 843 s, 824 m, 801 s, 760 m, 752 m, 739 s, 723 m, 712 s, 706 s, 693 s, 681 w, 662 w. ^{1}H NMR (δ, $CDCl_3$): 7.9–7.4 (m, 15 H, Ph), 5.29 (s, 1 H, CH_2Cl_2), 4.49 (s, 5 H, C_5H_5), 2.06 (s, 3 H, Me). FAB MS: 682, [M]$^+$, 51; 605*, [M – Ph]$^+$, 3; 593*, [M – CPh]$^+$, 5; 456*, $[Ru(CN)(PPh_3)(C_5H_5)]^+$, 15; 429*, $[Ru(PPh_3)(C_5H_5)]^+$, 100; 350*, $[Ru(PPh_2)(C_5H_5)]^+$, 14.

Shortening the duration of the reaction of $Ru[C{=}CMeC(CF_3)_2C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)$ in CH_3CN to 10 min (until all the starting material had dissolved) allowed the isolation of $Ru[C({=}C(CN)_2)CMe{=}C(CF_3)_2](NCMe)(PPh_3)(\eta\text{-}C_5H_5)$, which was purified by TLC (R_f 0.38; petroleum spirit/acetone/CH_3CN, 3:1:0.25) and precipitated from cyclohexane. Infrared (Nujol, cm^{-1}): ν(CN) 2268 w, 2238 w; ν(CC) 1690 w (br), 1659 w (br), 1592 w; ν(CF) 1288 (sh), 1221 vs, 1251 (sh), 1216 m, 1196 s, 1182 (sh); other peaks at 1483 m, 1439 (sh), 1435 m, 1377 m, 1160 w, 1145 w, 1137 w, 1095 m, 1029 w, 998 m, 936 m, 874 w, 847 w, 832 w, 801 w, 747 m, 719 m, 711 (sh), 700 (sh), 693 m, 688 (sh). ^{1}H NMR (δ, $CDCl_3$): 7.36–7.26 (m, 30 H, Ph), 4.54 (s, 5 H, C_5H_5), 1.81 (s, 3 H, CH_3CN), 1.11 (s, 3 H, Me). FAB MS: 723, [M]$^+$, 5; 682, [M – CH_3CN]$^+$, 23; 612*, [682 – CF_3]$^+$, 4; 605, [682 – Ph]$^+$, 5; 429*, $[Ru(PPh_3)(C_5H_5)]^+$, 100; 363*, $[Ru(PPh_3)]^+$, 11; 350*, $[Ru(PPh_2)(C_5H_5)]^+$, 21; 285*, $[Ru(PPh_2)]^+$, 10; 244, $[RuPh(C_5H_5)]^+$, 18; 167, $[Ru(C_5H_5)]^+$, 14.

Reaction of $Ru[C{=}CMeC(CF_3)_2C(CN)_2](PPh_3)_2(\eta\text{-}C_5H_5)$ (1d) with CO. A solution of **1d** (300 mg, 0.32 mmol) in tetrahydrofuran (20 mL) was carbonylated in an autoclave (50 atm of CO, 120 °C, 20 h). Separation on a silica TLC plate (1:1 diethyl ether/light petroleum) and crystallization (acetone/ethanol) gave two isomers of $Ru[C({=}C(CN)_2)CMe{=}C(CF_3)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$ (**2h**) as yellow crystals. (i) R_f = 0.7 (47 mg, 21%); mp 229–231 °C. Anal. Calcd for $C_{33}H_{23}F_6N_2OPRu$: C, 55.9; H, 3.3; N, 4.0; F, 16.1; M_r, 710. Found: C, 55.9; H, 3.0; N, 4.0; F, 16.0; M_r (mass spectrometry), 710. Infrared (CH_2Cl_2, cm^{-1}): ν(CO) 1975 vs. Infrared (Nujol, cm^{-1}): ν(CN) 2215 (sh), 2208 w, 2202 m; ν(CC) 1620 m; ν(CF, major peaks) 1345 s, 1253 s, 1140 s; other peaks at 1435 m, 1217 m, 1172 w, 1119 m, 1090 w, 1064 (sh), 1037 w, 1028 (sh), 967 m, 934 w, 843 w, 838 m, 831 m, 810 m, 750 m, 745 m, 717 m, 713 w, 702 (sh), 697 m, 639 w. ^{1}H NMR (δ, $CDCl_3$): 1.07 (m, 3 H, Me), 5.08 (s, 5 H, C_5H_5), 7.5 (m, 15 H, Ph). ^{13}C NMR (δ, $CDCl_3$): 18.2 (s, Me), 87.0 (s, diene skeleton), 89.8 (s, C_5H_5), 113.7, 118.5 (2 × s, CN), 128.7–136.4 (m, Ph), 167.9 (s, C_2), 203.9 (d, J(CP) = 18 Hz), 222.5 (d, J(CP) = 9 Hz) (CO, RuC); CF_3 resonances not observed. (ii) R_f = 0.5 (135 mg, 60%); mp 176–177 °C. Anal. Calcd for $C_{33}H_{23}F_6N_2OPRu$: C, 55.9; H, 3.3; N, 4.0; F, 16.1; M_r, 710. Found: C, 55.6; H, 3.0; N, 4.0; F, 15.8; M_r (mass spectrometry), 710. Infrared (CH_2Cl_2, cm^{-1}): ν(CO) 1969 vs. Infrared (Nujol, cm^{-1}): ν(CN) 2220 m, 2212 m; ν(CC) 1617 m; ν(CF, major bands) 1343 s, 1255 s, 1142 s; other bands at 3086 vw, 3058 vw, 1441 m, 1436 w, 1224 m, 1187 w, 1169 m, 1123 m, 1098 m, 1090 w, 1040 w, 1001 w, 966 m, 930 w, 852 w, 845 w, 832 m, 811 w, 754 (sh), 750 w, 748 m, 719 m, 709 m, 697 m, 639 w. ^{1}H NMR (δ, $CDCl_3$): 1.84 (m, 3 H, Me), 5.03 (s, 5 H, C_5H_5), 7.45 (m, 15 H, Ph). ^{13}C NMR (δ, $CDCl_3$): 21.8 (s, Me), 89.8 (s, C_5H_5), 106.7 (s), 108.3 (m), 109.8 (m), 112.6 (s), 115.2 (m), 117.2 (s) (a mixture of CF_3, diene, and CN resonances), 128.7–135.3 (m, Ph), 166.5 (s, C(2)), 207.7 (d, J(CP) = 18 Hz), 219.3 (d, J(CP) = 9 Hz) (CO, RuC).

Table V. Fractional Atomic Coordinates (×10^4 for All Atoms) for $Ru[C({=}C(CN)_2)CMe{=}C(CF_3)_2](CO)(PPh_3)(\eta\text{-}C_5H_5)$ (2h)

atom	*x*	*y*	*z*
Ru	3167 (1)	4441 (1)	6801 (1)
P(1)	1928 (1)	4758 (1)	6044 (1)
F(1)	2622 (2)	5842 (2)	8152 (3)
F(2)	3074 (3)	6816 (2)	8867 (3)
F(3)	2304 (3)	6820 (3)	7416 (3)
F(4)	3407 (4)	7660 (3)	7949 (5)
F(5)	3811 (4)	7181 (3)	7246 (5)
F(6)	4465 (4)	7246 (3)	8692 (5)
O(1)	3427 (3)	5525 (3)	5776 (4)
N(1)	4424 (3)	5650 (3)	10272 (4)
N(2)	3569 (5)	3567 (3)	9277 (5)
C(1)	3370 (2)	3303 (2)	7349 (2)
C(2)	2928 (2)	3269 (2)	6402 (2)
C(3)	3313 (2)	3550 (2)	6079 (2)
C(4)	3994 (2)	3757 (2)	6826 (2)
C(5)	4029 (2)	3604 (2)	7611 (2)
C(6)	3557 (3)	5050 (3)	7997 (4)
C(7)	3823 (3)	5789 (3)	8015 (4)
C(8)	3516 (4)	6400 (3)	8015 (4)
C(9)	3757 (3)	4817 (3)	8839 (4)
C(10)	4134 (3)	5285 (3)	9642 (4)
C(11)	3637 (4)	4118 (4)	9056 (5)
C(12)	4540 (4)	5778 (4)	8091 (5)
C(13)	2878 (4)	6466 (4)	8094 (5)
C(14)	3796 (6)	7109 (4)	7971 (7)
C(15)	3299 (3)	5154 (3)	6180 (4)
C(21)	1592 (2)	5601 (2)	5387 (2)
C(22)	2047 (2)	6191 (2)	5674 (2)
C(23)	1779 (2)	6837 (2)	5220 (2)
C(24)	1055 (2)	6893 (2)	4480 (2)
C(25)	600 (2)	6303 (2)	4193 (2)
C(26)	868 (2)	5657 (2)	4647 (2)
C(27)	1337 (2)	4089 (2)	5143 (3)
C(28)	826 (2)	3691 (2)	5168 (3)
C(29)	434 (2)	3160 (2)	4524 (3)
C(30)	555 (2)	3027 (2)	3855 (3)
C(31)	1067 (2)	3424 (2)	3830 (3)
C(32)	1458 (2)	3956 (2)	4474 (3)
C(33)	1558 (2)	4789 (2)	6742 (2)
C(34)	1032 (2)	5281 (2)	6579 (2)
C(35)	756 (2)	5269 (2)	7105 (2)
C(36)	1006 (2)	4767 (2)	7795 (2)
C(37)	1532 (2)	4275 (2)	7958 (2)
C(38)	1808 (2)	4286 (2)	7431 (2)

Single-Crystal X-ray Diffraction Studies of 1g, 2g, 2h, and 3g. Intensity data for the four samples were measured at room temperature on an Enraf-Nonius CAD4F diffractometer fitted

Table VI. Fractional Atomic Coordinates ($\times 10^5$ for Ru; $\times 10^4$ for Other Atoms) for $Ru[\eta^3\text{-}C(CF_3)_2CPhC{=}C(CN)_2](PPh_3)(\eta\text{-}C_5H_5) \bullet H_2O$ (3g)

atom	x	y	z
Ru	-11337 (4)	19361 (3)	14673 (4)
P(1)	-2239 (1)	1026 (1)	2045 (1)
F(1)	-442 (3)	1521 (3)	3894 (3)
F(2)	-1599 (4)	2317 (4)	4026 (4)
F(3)	-114 (5)	2622 (4)	4498 (4)
F(4)	-1836 (4)	3556 (3)	2755 (5)
F(5)	-656 (4)	3780 (3)	1964 (4)
F(6)	-426 (4)	3863 (3)	3500 (4)
N(1)	2507 (6)	1119 (6)	3200 (6)
N(2)	504 (6)	-373 (6)	1315 (7)
C(1)	-1927 (7)	2843 (5)	461 (6)
C(2)	-940 (7)	2742 (5)	265 (6)
C(3)	-826 (7)	1963 (5)	-48 (5)
C(4)	-1715 (6)	1569 (6)	-39 (5)
C(5)	-2385 (7)	2121 (5)	276 (6)
C(6)	117 (5)	1497 (5)	2114 (5)
C(7)	191 (5)	2299 (4)	2344 (5)
C(8)	-624 (5)	2591 (4)	2801 (5)
C(9)	811 (5)	921 (5)	2193 (6)
C(10)	1761 (7)	1025 (5)	2749 (7)
C(11)	640 (6)	203 (6)	1687 (7)
C(12)	1043 (4)	2755 (3)	2093 (3)
C(13)	-703 (6)	2274 (5)	3796 (6)
C(14)	-877 (7)	3444 (5)	2744 (7)
C(15)	1478 (4)	3311 (3)	2744 (3)
C(16)	2329 (4)	3687 (3)	2570 (3)
C(17)	2746 (4)	3507 (3)	1746 (3)
C(18)	2311 (4)	2951 (3)	1095 (3)
C(19)	1460 (4)	2575 (3)	1269 (3)
C(21)	-1849 (4)	426 (3)	3134 (3)
C(22)	-1073 (4)	-93 (3)	3141 (3)
C(23)	-788 (4)	-559 (3)	3951 (3)
C(24)	-1279 (4)	-506 (3)	4753 (3)
C(25)	-2056 (4)	12 (3)	4746 (3)
C(26)	-2340 (4)	478 (3)	3936 (3)
C(27)	-2646 (3)	307 (3)	1083 (4)
C(28)	-2015 (3)	-295 (3)	923 (4)
C(29)	-2264 (3)	-798 (3)	142 (4)
C(30)	-3144 (3)	-699 (3)	-478 (4)
C(31)	-3776 (3)	-97 (3)	-318 (4)
C(32)	-3527 (3)	406 (3)	462 (4)
C(33)	-3412 (4)	1425 (2)	2292 (4)
C(34)	-4176 (4)	929 (2)	2435 (4)
C(35)	-5052 (4)	1232 (2)	2658 (4)
C(36)	-5164 (4)	2032 (2)	2739 (4)
C(37)	-4400 (4)	2528 (2)	2597 (4)
C(38)	-3524 (4)	2224 (2)	2373 (4)
O(w)	680 (4)	4495 (3)	523 (5)

with Mo K$\bar{\alpha}$ (graphite monochromator) radiation (λ = 0.710 73 Å) with the use of the $\omega/2\theta$ scan technique ($\omega/(^4/_3\theta)$ scan technique was used for **2h**). The intensities of three standard reflections were measured after every 3600 s of X-ray exposure time for each compound, and these indicated that no significant decomposition of any of the crystals occurred during their respective data collections. Routine corrections were made for Lorentz and polarization effects and for absorption[22] (see ref 23 for **2h**). Relevant crystal data are summarized in Table II.

The position of the Ru atom in each of the structures was obtained from the interpretation of the Patterson synthesis; all other non-hydrogen atoms were located from subsequent difference maps. The structures were refined by a full-matrix least-squares procedure based on F.[22] In the refinement of the structures, the phenyl rings were constrained as hexagonal rigid groups and, in addition, the cyclopentadienyl ring in **2h** was refined as a rigid group. The remaining non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were included in the models at their calculated positions. A weighting scheme of the form $w = k/[\sigma^2(F) + gF^2]$ was included, and the refinement was continued until convergence in each case. The absolute configuration of **1g** was determined on the basis of differences in Friedel pairs included in the data set. Final refinement details are listed in Table II. Listings of fractional atomic coordinates are given in Tables III–VI and the numbering schemes used are shown in Figures 1–4, which were drawn with 15% probability ellipsoids by the use of ORTEP.[24] Selected interatomic parameters for the four complexes are given in Table I.

Scattering factors for neutral Ru (corrected for f' and f'') were from ref 25, and values for the remaining atoms were those incorporated in SHELX.[22] Data solution and refinement were performed with the SHELX program system on the University of Adelaide's VAX11/785 and CYBER (for **2h**) computer systems.

Acknowledgment. This work was supported by grants (to M.I.B. and M.R.S.) from the Australian Research Grants Scheme. A.G.S. and M.J.L. held Commonwealth Post-Graduate Research Awards.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond distances and angles, and hydrogen atom parameters for **1g**, **2g**, **2h**, and **3g** (19 pages); listings of observed and calculated structure factors (71 pages). Ordering information is given on any current masthead page.

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