kenes.[15] Interestingly, basic sites or additives are frequently found in the hetereogeneous metal-based catalysts used to process coal- and petroleum-derived feedstocks.[16] Thus, analogous acid/base chemistry of intermediate catalyst/alkene complexes may occur. Additional examples of vinylic deprotonations of alkene complexes will be reported in the near future.[17]

Acknowledgment. We thank the DOE for support of this research, the University of Utah for a Graduate Research Fellowship (T.-S.P.) and J. J. Kowalczyk for the discovery of the title reaction with another class of alkene complexes.[17]

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[15] Brandsma, L.; Verkruijsse, H. D.; Schade, C.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1986**, 260.

[16] E.g.: Lamb, H. H.; Gates, B. C. *J. Am. Chem. Soc.* **1986**, *108*, 81.

[17] Kowalczyk, J. J.; Arif, A. M.; Gladysz, J. A. Submitted for publication.

Articles

Cyclopentadienylruthenium and -osmium Chemistry. 33.[1] Cyclobutenyl–Nitrile Complexes. X-ray Structures of $Ru[C{=}CPhC(CF_3)_2C(CN)_2](NCMe)(PPh_3)(\eta\text{-}C_5H_5)$ and $[Ru[C{=}CPhC(CF_3)_2C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)]_2[\mu\text{-}(NC)_2C{=}C(CF_3)_2]$

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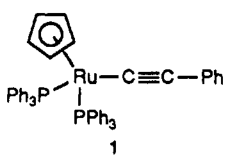
Replacement of MeCN in $Ru[C{=}CPhC(CF_3)_2C(CN)_2](NCMe)(PPh_3)(\eta\text{-}C_5H_5)$, readily obtained from the bis-PPh_3 complex in MeCN, by a series of organonitrile ligands ($CH_2{=}CHCN$, *trans*-$CH(CH){=}CH(CN)$, $C(CN)_2{=}C(CF_3)_2$ (dcfe), $C_2(CN)_4$, *o*-$C_6H_4(CN)_2$, *p*-$C_6H_4(CN)_2$, *o*-$C_6F_4(CN)_2$, *p*-$C_6F_4(CN)_2$, $C_6H_2(CN)_4$) has given highly colored complexes containing one or two $Ru[C{=}CPhC(CF_3)_2C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)$ moieties. The binuclear complexes are bridged by the di- or tetranitriles; isomers were found for the fumaronitrile, dcfe, and $C_2(CN)_4$ derivatives. The deep blue μ-dcfe complexes are readily oxidized to green paramagnetic species that appear to contain an epoxy radical ligand. The complexes were characterized by spectroscopic and electrochemical studies and, in the case of the title complexes, by single-crystal X-ray diffraction studies. Crystals of $Ru[C{=}CPhC(CF_3)_2C(CN)_2](NCMe)(PPh_3)(\eta\text{-}C_5H_5)$ (4) crystallize in the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 13.682$ (2) Å, $b = 15.616$ (2) Å, $c = 9.776$ (4) Å, $\alpha = 97.97$ (4)°, $\beta = 92.90$ (3)°, and $\gamma = 80.53$ (2)° with $Z = 2$. Crystals of $[Ru[C{=}CPhC(CF_3)_2C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)]_2[\mu\text{-}(NC)_2C{=}C(CF_3)_2]$ (**2a**) are monoclinic, space group $P2_1/c$, with unit cell parameters $a = 20.48$ (1) Å, $b = 19.378$ (4) Å, $c = 20.914$ (3) Å, $\beta = 112.6$ (3)°, and $Z = 4$. The structures were refined by a full-matrix (blocked-matrix for **2a**) least-squares procedure to final $R = 0.059$ and $R_w = 0.064$ for 3883 reflections with $I \geq 2.5\sigma(I)$ for 4 and $R = 0.045$ and $R_w = 0.045$ for 1708 reflections for **2a**.

Introduction

We have recently described some cycloaddition reactions of 1,1-dicyano-2,2-bis(trifluoromethyl)ethene, $(CF_3)_2C{=}C(CN)_2$ (dcfe), with transition-metal σ-acetylide complexes to give a series of cyclobutenyl, butadienyl, and allyl compounds.[2] En passant, we reported the reaction between dcfe and $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (1), which afforded a deep blue binuclear complex that showed a weak paramagnetism (a broad ESR signal arising from ca. 0.04 unpaired electron per molecule). The complex was characterized by a single-crystal X-ray study, which revealed the binuclear structure 2, only consistent with a diamagnetic electronic structure. In the course of resolving this problem, we have made and characterized several related complexes containing a variety of organonitriles. This



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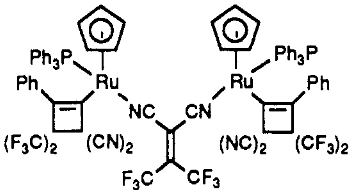

2a

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[1] Part 32: Bruce, M. I.; Cifuentes, M. P.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1989**, *359*, 379.

[2] Bruce, M. I.; Hambley, T. W.; Liddell, M. J.; Snow, M. R.; Swincer, A. G.; Tiekink, E. R. T. *Organometallics* **1990**, *9*, 96.

Table I. ^{1}H and ^{19}F NMR Data for the Nitrile Complexes

compd	^{1}H NMR, δ	^{19}F NMR, δ
dcfe		$CDCl_3$: −61.8 (s, CF_3)
4	$CDCl_3$: 7.4–6.5 (m, 20 H, Ph); 5.27 (s, 1.5 H, CH_2Cl_2); 4.41 (s, 5 H, C_5H_5); 1.95 (d, J_{P-H} = 1.2 Hz, 3 H, MeCN)	$CDCl_3$: −66.2 (q, J_{F-F} = 10 Hz, CF_3); −66.4 (q, J_{F-F} = 10 Hz, CF_3)
5	$CDCl_3$: 7.4–6.5 (m, 20 H, Ph); 5.74 (m, 1 H, CH); 5.55 (m, 2 H, CH_2); 4.50 (s, 5 H, C_5H_5)	not recorded
6	C_6D_6: 7.2–6.5 (m, 22 H, Ph + C_6H_2); 4.82 (s, 5 H, C_5H_5); 4.30 (s, 1 H, CH_2Cl_2)	$CDCl_3$: −66.1 (q, J_{F-F} = 10 Hz, CF_3); −66.5 (q, J_{F-F} = 10 Hz, CF_3)
7	$CDCl_3$: 7.6–6.5 (m, 24 H, Ph + C_6H_4); 4.67 (s, 5 H, C_5H_5)	$CDCl_3$: −66.1 (m, unresolved, CF_3); −66.4 (m, unresolved, CF_3)
11	C_6D_6: 7.1–6.5 (m, 20 H, Ph); 4.82 (s, 5 H, C_5H_5)	$CDCl_3$: −66.1 (q, J_{F-F} = 9 Hz, 3 F, CF_3); −66.4 (q, J_{F-F} = 11 Hz, 3 F, CF_3); −127.3 (m, 1 F, $F_{3,6}$); −128.3 (m, 1 F, $F_{3,6}$); −142.0 (m, 1 F, $F_{4,5}$); −144.5 (m, 1 F, $F_{4,5}$)
8	$CDCl_3$: 7.4–6.4 (m, 20 H, Ph); 4.70 (s, 5 H, C_5H_5)	$CDCl_3$: −66.1 (q, J_{F-F} = 10 Hz, 3 F, CF_3); −66.4 (q, J_{F-F} = 9 Hz, 3 F, CF_3); −128.7 (d, J_{F-F} = 14 Hz, 2 F, $F_{3,5}$); −130.5 (dd, J_{F-F} = 23, 8 Hz, 1 F, $F_{2,6}$); −131.4 (dd, J_{F-F} = 23, 11 Hz, 1 F, $F_{2,6}$)
9	$CDCl_3$: 7.4–6.5 (m, 20 H, Ph); 6.03 (d, J_{H-H} = 17 Hz, 1 H, CH); 5.49 (d, J_{H-H} = 17 Hz, 1 H, CH); 4.56 (s, 5 H, C_5H_5)	$CDCl_3$: −66.2 (q, J_{F-F} = 10 Hz, CF_3); −66.4 (q, J_{F-F} = 11 Hz, CF_3)
12	C_6D_6: 7.1–6.5 (m, 40 H, Ph); 5.01 (s, 10 H, C_5H_5)	$CDCl_3$: −66.1 (q, J_{F-F} = 11 Hz, 6 F, CF_3); −66.4 (q, J_{F-F} = 10 Hz, 6 F, CF_3); −128.7 (d, J_{F-F} = 14 Hz, 2 F, $F_{3,6}$); −145.5 (d, J_{F-F} = 11 Hz, 2 F, $F_{4,5}$)
10a	$CDCl_3$: 7.4–6.4 (m, 40 H, Ph); 5.30 (s, 2 H, CH_2Cl_2); 5.14 (s, 2 H, CH); 4.56 (s, 10 H, C_5H_5)	$CDCl_3$: −66.1 (q, $J_{F,F}$ = 10 Hz, CF_3); −66.4 (q, J_{F-F} = 10 Hz, CF_3)
10b	$CDCl_3$: 7.3–6.5 (m, 40 H, Ph); 5.30 (s, 3 H, CH_2Cl_2); 5.29 (s, 2 H, CH); 4.57 (s, 10 H, C_5H_5)	$CDCl_3$: −66.1 (q, J_{F-F} = 10 Hz, CF_3); −66.4 (q, J_{F-F} = 10 Hz, CF_3)
13a	C_6D_6: 7.4–6.4 (m, 40 H, Ph); 4.94 (s, 10 H, C_5H_5)	$CDCl_3$: −65.8 (q, J_{F-F} = 10 Hz, CF_3); −66.4 (q, J_{F-F} = 10 Hz, CF_3)
13b	C_6D_6: 7.2–6.5 (m, 40 H, Ph); 4.99 (s, 10 H, C_5H_5); 4.50 (s, 1 H, CH_2Cl_2)	$CDCl_3$: −65.7 (m, unresolved, CF_3); −66.4 (m, unresolved, CF_3)
13c	C_6D_6: 7.1–6.4 (m, 40 H, Ph); 4.78 (d, J_{P-H} = 1 Hz, 10 H, C_5H_5)	$CDCl_3$: −66.0 (q, J_{F-F} = 12 Hz, CF_3); −66.4 (q, J_{F-F} = 11 Hz, CF_3)
2a	C_6D_6: 7.2–6.4 (m, 40 H, Ph); 5.03 (s, 10 H, C_5H_5)	$CDCl_3$: −61.5 (s, 6 F, dcfe); −66.0 (q, J_{F-F} = 10 Hz, 6 F, CF_3); −66.4 (q, J_{F-F} = 10 Hz, 6 F, CF_3)
2b	C_6D_6: 7.4–6.4 (m, 40 H, Ph); 4.81 (s, 10 H, C_5H_5)	$CDCl_3$: −59.8 (s, 6 F, dcfe); −65.8 (q, J_{F-F} = 10 Hz, 6 F, CF_3); −66.3 (q, J_{F-F} = 10 Hz, 6 F, CF_3)
15b	$CDCl_3$: no signals	not recorded

paper describes this chemistry, together with the X-ray structural studies of the title complexes.

Results and Discussion

The original synthesis of **2** was from dcfe and **1** in benzene. If the reaction was carried out in acetonitrile, a precipitate of $Ru[C{=}CPhC(CF_3)_2C(CN)_2](PPh_3)_2(\eta\text{-}C_5H_5)$ (**3**) was obtained; this was then collected and suspended in acetonitrile for 1.5 days, forming a pale yellow solution from which the yellow crystalline $Ru[C{=}CPhC(CF_3)_2C(CN)_2](NCMe)(PPh_3)(\eta\text{-}C_5H_5)$ (**4**) was isolated in 43% yield. Complex **4** was characterized by analytical and spectroscopic data (Table I). In the FAB mass spectrum a molecular ion was found at m/z 785, which fragmented by loss of MeCN, CN, CF_3, and phenyl groups. A weak ion was found at m/z 530 corresponding to $[M - MeCN - dcfe]^+$, allowing the identification of **4** as a cyclobutenyl complex.[2] The IR spectrum of **4** shows ν(CN) bands at 2267 and 2235 cm^{-1} of medium and weak intensities, respectively, and ν(C=C) bands at 1613, 1590, and 1576 cm^{-1}. Other bands attributable to ν(CF) absorptions were found between 1099 and 1310 cm^{-1}. In the ^{1}H NMR spectrum a doublet signal at δ 1.95 (J_{PH} = 1.2 Hz) was found for the CH_3 group and a singlet at δ 4.41 for the η-C_5H_5 group, while a series of resonances between δ 6.5 and 7.4 were attributable to the phenyl groups. The ^{19}F resonances at δ −66.2 and −66.4 showed that the two CF_3 groups were inequivalent in solution. An X-ray structure determination of **4** has been performed, which confirms the mononuclear structure expected from spectroscopic data.

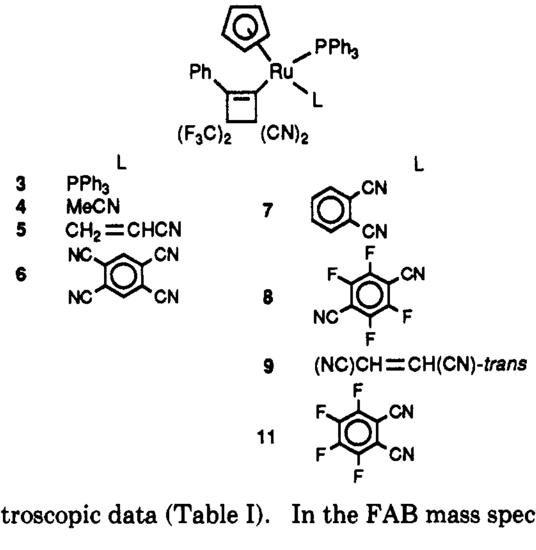

Figure 1 shows a plot of the molecular structure of **4**, and significant bond distances are listed in Table II. Complex **4** is chiral at the ruthenium, with both enantiomers being found in the unit cell. The ruthenium atom is coordinated to MeCN (Ru–N(1) = 2.033 (6) Å), PPh_3 (Ru–P = 2.297 (2) Å), and C_5H_5 ligands (Ru–C(cp) = 2.191 (7)–2.243 (8) Å, average 2.224 Å), all distances being within the ranges normally found for complexes containing these ligands.[3] The cyclobutenyl ligand occupies the remaining

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[3] Bruce, M. I.; Hambley, T. W.; Snow, M. R.; Swincer, A. G. *J. Organomet. Chem.* **1982**, *235*, 105. Robinson, V.; Taylor, G. E.; Woodward, P.; Bruce, M. I.; Wallis, R. C. *J. Chem. Soc., Dalton Trans.* **1981**, 1169.

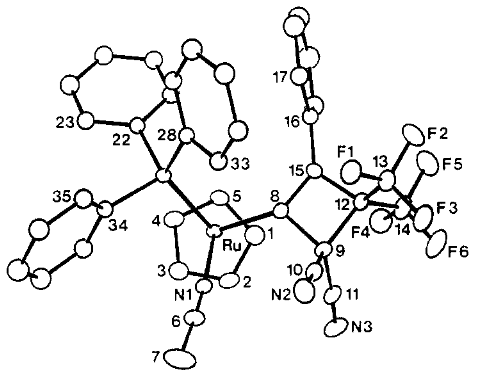
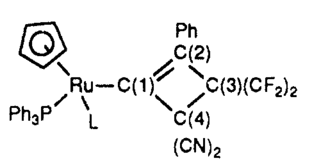


Figure 1. ORTEP view of $Ru[\overline{C{=}CPhC(CF_3)_2C}(CN)_2](NCMe)(PPh_3)(\eta\text{-}C_5H_5)$ (4) showing the atom-labeling scheme. Atoms not otherwise indicated are carbons.

Table II. Selected Bond Distances (Å) and Angles (deg) for $Ru[C{=}CPhC(CF_3)_2C(CN)_2](L)(PPh_3)(\eta\text{-}C_5H_5)$



	L = CO	L = NCMe	L = $^1/_2$ $(NC)_2C{=}C(CF_3)_2$
Ru-C(cp) (av)	2.258	2.224	2.23
Ru-CO	1.839 (9)		
Ru-N		2.033 (6)	1.98 (1), 1.98 (2)
Ru-P	2.309 (2)	2.297 (2)	2.314 (6), 2.316 (6)
Ru-C(1)	2.054 (8)	2.034 (7)	2.07 (2), 2.01 (2)
C(1)-C(2)	1.35 (1)	1.359 (9)	1.30 (3), 1.39 (3)
C(2)-C(3)	1.53 (1)	1.53 (1)	1.53 (3), 1.55 (4)
C(3)-C(4)	1.57 (1)	1.58 (1)	1.53 (3), 1.67 (3)
C(4)-C(1)	1.57 (1)	1.58 (1)	1.60 (3), 1.67 (3)
Ru-C(1)-C(2)	140.9 (6)	139.7 (5)	143 (1), 141 (2)
Ru-C(1)-C(4)	126.1 (6)	126.7 (5)	126 (1), 126 (2)
C(2)-C(1)-C(4)	91.0 (6)	90.8 (6)	91 (2), 91 (2)
C(1)-C(2)-C(3)	97.3 (6)	97.5 (5)	97 (2), 99 (2)
C(2)-C(3)-C(4)	84.8 (6)	84.7 (5)	86 (1), 85 (2)
C(1)-C(4)-C(3)	86.8 (6)	86.9 (5)	86 (1), 99 (2)
L-Ru-P	90.9 (2)	88.0 (2)	91.2 (5), 92.6 (5)
L-Ru-C(1)	92.2 (3)	88.2 (2)	91.8 (7), 89.0 (8)
P-Ru-C(1)	95.9 (2)	95.7 (2)	96.0 (5), 95.2 (6)

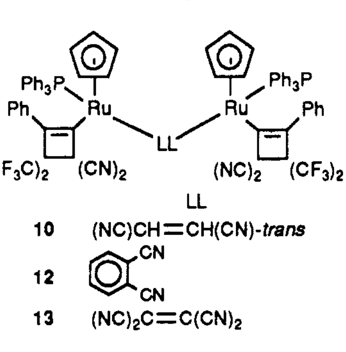
coordination position of the distorted-octahedral geometry; the Ru-C(8) separation (2.034 (7) Å) is similar to that found in 3.

The room-temperature reaction of a benzene solution of 4 with dcfe gave us a new route to the synthesis of pure, diamagnetic $[Ru[C{=}CPhC(CF_3)_2C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)]_2[\mu\text{-}(NC)_2C{=}C(CF_3)_2]$ (**2a**). Unit cell parameters for **2a** were in good agreement with the crystallographically characterized complex. An isomer, **2b**, was isolated with use of different chromatographic procedures. Isomers **2a** and **2b** do not appear to interconvert in solution, since no extra peaks were observed in the ^1H NMR spectra of **2a** after 7 days in a benzene-d_6 solution. The dcfe derivatives are soluble in hydrocarbon solvents, their IR spectra showing only two bands in the ν(CN) region, while in Nujol mulls complex four-band ν(CN) patterns were found. The presence of four bands instead of two is probably due to solid-state and/or solution effects.[4]

In the ^1H NMR spectrum of **2a**, one η-C_5H_5 resonance was found at δ 5.03, demonstrating the equivalence of the two cyclopentadienyl ligands in solution. This is confirmed by the solid-state structure of **2a**, which shows the cyclopentadienyl groups in similar environments. Only two CF_3 signals (δ -66.0, -66.4), assigned to the ring CF_3 groups, were found in the ^{19}F NMR spectrum of **2a**. This is consistent with the chiral nature of the complex, showing that the two cyclobutenyl rings are equivalent in solution and the two CF_3 groups within each cyclobutenyl ring are inequivalent. The CF_3 groups on the bridging nitrile gave rise to a signal at δ -61.5. Similarly, two CF_3 signals were found for the cyclobutenyl CF_3 groups in **2b** at δ -65.8 and -66.3, and one signal for the bridging ligand was located at δ -59.8. Molecular ions were found in the FAB mass spectra at m/z 1703 for both **2a** and **2b**. Oxidation processes were observed for the compounds **2a** and **2b**, where $[M + O]^+$ ions were found at m/z 1720. The relative abundance of these ions is initially comparable to that of $[M]^+$ but increases with time (see below).

The X-ray structure of **2a** is shown in Figure 2, and bond distances are shown in Table II. The ruthenium atoms have pseudooctahedral geometry, and the cyclopentadienyl and triphenylphosphine ligands have normal bonding distances (Ru(1)-P(1) = 2.314 (6) Å, Ru(2)-P(2) = 2.316 (6) Å; Ru-C(cp) = 2.20 (1)-2.27 (2) Å, average 2.23 Å). The observed Ru-C(sp^2) distances (Ru(1)-C(24) = 2.07 (2) Å, Ru(2)-C(61) = 2.01 Å) are similar to those found earlier.[2] Each ruthenium center is chiral; both enantiomers of the molecule shown are present in the unit cell. The differences in C-C distances between the cyclobutenyl rings are within 3σ, the esd's being rather high. The most notable feature of the structure is the presence of the bridging dcfe group. The Ru-N distances (Ru(1)-N(5) = 1.98 (1) Å, Ru(2)-N(6) = 1.98 (2) Å) are slightly shorter than that observed for 4 (Ru-N(1) = 2.033 (6) Å). This suggests stronger bonding, but because of the large esd's, the differences may not be significant.

The reactions of the nitriles acrylonitrile, 1,2,4,5-$C_6H_2(CN)_4$, o-$C_6H_4(CN)_2$, and p-$C_6F_4(CN)_2$ with 4 in benzene at room temperature gave the mononuclear complexes 5-8, respectively. Partially characterized binuclear complexes were also obtained from the tetrafluoroterephthalonitrile and tetracyanobenzene reactions, spectroscopic data for these being reported below. Both mononuclear and binuclear complexes were isolated from the reactions of 4 with the dinitriles *trans*-CH(CN)=CH(CN) and p-$C_6F_4(CN)_2$ in benzene. A mononuclear product (**9**) and two isomeric binuclear products (**10a,b**) were obtained from the fumaronitrile system. The tetrafluorophthalonitrile reaction gave a mononuclear complex (**11**) and a binuclear complex (**12**). Only binuclear complexes were isolated from the reaction of tetracyanoethene (tcne) with 4, three isomers (**13a-c**) being obtained.



The mononuclear and binuclear complexes from these reactions were characterized by microanalysis, FAB mass spectrometry, electrochemistry, and, where appropriate, by ^1H and ^{19}F NMR spectroscopy. The spectral properties

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[4] Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: New York, 1975; p 145.

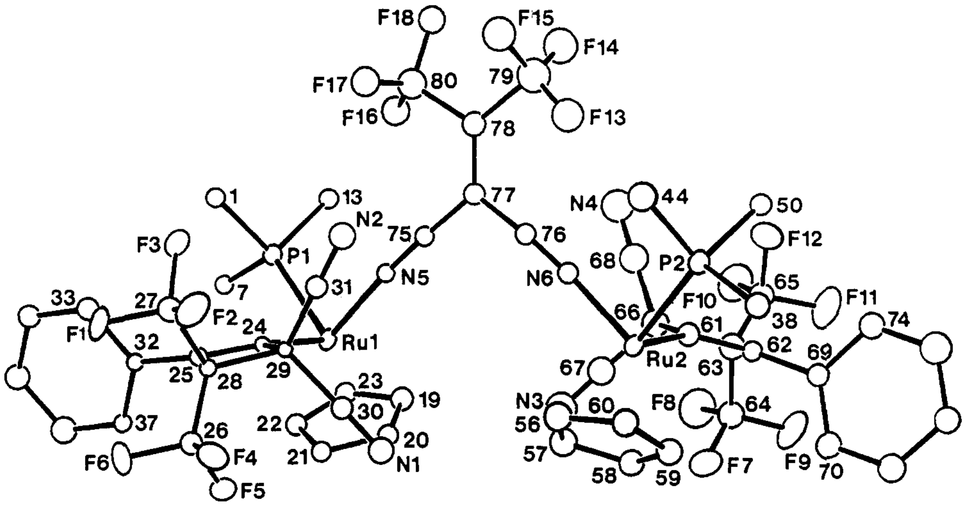
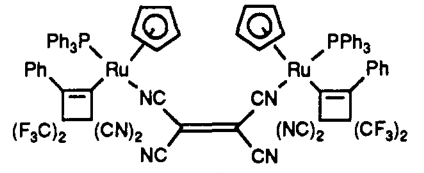


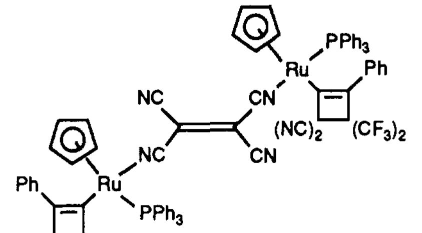
Figure 2. ORTEP view of $[Ru[C{=}CPhC(CF_3)_2C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)]_2[\mu\text{-}(NC)_2C{=}C(CF_3)_2]$ (**2a**) showing the atom-labeling scheme. Atoms not otherwise indicated are carbons. For clarity, only ipso carbon atoms of the P-bonded phenyl groups are shown.

of complexes **5**–**8** and **11** (see Table I) are similar to those of **4** and suggest that related structures are likely for these complexes, with a $\eta^1(N)$-bound nitrile ligand attached to the $Ru[C{=}CPhC(CF_3)_2C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)$ core. Similarly, the spectral data for the binuclear complexes **10**, **12**, and **13** (Table I) show that they have structures related to that of **2a**.

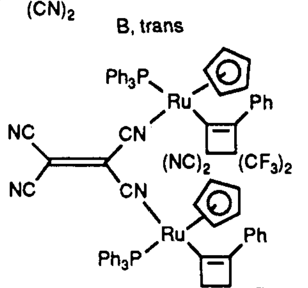
For tcne the possibility of cis, trans, and gem isomers also exists, as well as orientational isomerism. The alternative isomeric possibilities are illustrated for the tcne structures A–C.



A, cis



B, trans



C, gem

In the case of the fumaronitrile and dcfe ligands it is probably not the olefin itself that is responsible for the isomerism but alternative orientations of the ruthenium centers arising from interactions between the phosphine and cyclobutenyl ligands.

The IR data for the mononuclear complexes **5**–**9** and **11** were similar to those of **4**. Very weak ν(CN) bands were observed between 2220 and 2250 cm^{-1} for the ring CN groups and medium- to strong-intensity bands for the nitrile ligands (2170–2270 cm^{-1}), the more electron-deficient ligands having the lower ν(CN) stretching frequencies. The ν(C=C) bands varied in intensity from very weak to strong, with contributions from the double bonds of the nitrile ligands evident in several of the spectra (e.g. 1574 s (**5**), 1590 m (**9**) cm^{-1}). Strong ν(CF) bands were found for all complexes in the range 1088–1310 cm^{-1}. The IR spectra of the binuclear complexes have slightly less intense ν(C=C) bands than their mononuclear counterparts but are otherwise very similar. The ν(CN) bands were shifted to higher frequency (by 2–40 cm^{-1}) and were fewer in number and/or had smaller line widths (indicative of fewer overlapping bands) than the mononuclear derivatives.

An examination of the stronger ν(CN) bands (2200–2010 cm^{-1}) for the binuclear complexes has suggested a correlation between the number of bands observed and the symmetry of the products. For the isomers of **10**, the one-band pattern suggests a highly symmetrical orientation of the two $Ru[C{=}CPhC(CF_3)_2C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)$ groups. In the case of the tcne derivatives, two of the isomers (**13a**,**b**) have a two-band pattern, while the third isomers (**13c**) has a one-band pattern. It seems likely that the third isomer has a trans symmetry similar to the isomers of **10**.

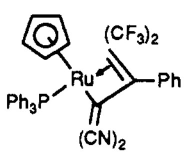
Cyclopentadienyl resonances were observed in the ^{1}H NMR spectra of complexes **5**–**9** and **11** (Table I). As expected, the effect of increasing the electron deficiency of the nitrile ligands was to shift the cyclopentadienyl resonance downfield (e.g. δ 4.82 for **6** and δ 4.82 for **11**, versus δ 4.41 for **4**). A mononuclear formulation was assigned to **9** on the basis of the ^{1}H NMR spectrum: signals were found for the two CH groups in the fumaronitrile ligand at δ 5.49 and 6.03 and for the cyclopentadienyl group at δ 4.56, respectively (relative intensities 1/1/5). Complex **5** had ^{1}H NMR signals assigned to the $C\mathit{H}(CN)$ (δ 5.74) and $C\mathit{H}_2{=}$ (δ 5.55) protons of the acrylonitrile ligand and to the η-C_5H_5 group (δ 4.50); these signals had intensities in the ratio 1/2/5. The ^{1}H NMR spectra of the binuclear compounds were similar to that of **2a** and show that the two cyclopentadienyl ligands in each complex are equivalent in solution. Integration of the CH/C_5H_5 signals (2/10) for each of the isomers of **10** confirmed their binuclear formulations.

The ^{19}F NMR spectra (Table I) showed that the CF_3 groups in all complexes are inequivalent, with two quartets for each complex found between δ −65.7 and −66.5. As noted above, this is indicative of a chiral metal center that creates different CF_3 environments on either side of the cyclobutenyl ring. Complex 8 was shown to have a mononuclear formulation by comparison of the two CF_3 quartets (δ −66.1 and −66.4) with the signals observed at higher field for the $C_6F_4(CN)_2$ ligand (intensities 3/3/4). Comparison of the signals for the fluorines in the coordinated ntirile and in the free ligand (δ −130.6) showed that F_2 and F_6 are inequivalent (δ −130.5, −131.4) and are shifted upfield slightly, while F_3 and F_4 are deshielded (δ −128.7). The spectrum of 11 showed signals for the CF_3 groups in the normal region (δ −66.1, −66.4), while the aromatic nitrile ligand displayed signals for F_3 and F_6 (δ −127.3, −128.3) and for F_4 and F_5 (δ −142.0, −144.5).

The signals observed for the fluoro nitrile ligands in 8 and 11 result from fluorine–fluorine (including cross-ring) coupling and from coupling to phosphorus: the expected AA′XX′Y systems were not fully resolved. The ^{19}F spectra of complexes **10**, **12**, and **13** were similar to that of **2a**. The tetrafluorophthalonitrile derivative 12 was given a binuclear formulation by comparison of the CF_3 and C_6F_4 integrals (6/6/4). Two doublets were observed for the $C_6F_4(CN)_2$ group at δ −128.7 and −145.5 (J_{av} = 13 Hz). These were assigned to F_3, F_6 and F_4, F_5, respectively. The binuclear complex formed from the reaction of tetrafluoroterephthalonitrile with 4 showed a doublet signal for the C_6F_4 group at δ −132.7 (J = 14 Hz), which is again upfield from the free ligand (δ −130.6) and demonstrates that all fluorines are equivalent. The CF_3 and C_6F_4 signals had the relative intensities 6/6/4. A small difference in chemical shifts between the mononuclear and binuclear complexes of a given series was noted, the shifts for the mononuclear fluoronitrile ligands being at a lower field (1–2 ppm) than those of the binuclear complexes.

The fast atom bombardment (FAB) spectra for the mononitrile complexes are somewhat confusing, as ion/molecule aggregates are formed at higher mass. The principal aggregate $[M_2 - \text{nitrile}]^+$ appears to be formed by intermolecular association. This illustrates the problems that are faced in assigning molecular ions in complexes containing relatively labile ligands. The FAB mass spectra of the binuclear complexes showed weak molecular ions and fragmentation patterns similar to those of the mononuclear derivatives. The ion $[M - CCPhC(CF_3)_2C(CN)_2]^+$ was found only in the binuclear complexes. The ion $[M - \text{nitrile} - \text{dcfe}]^+$ (m/z 530), characteristic of the presence of the cyclobutenyl ligand,[2] was also found here in the spectra of all the mononuclear and binuclear complexes.

In all spectra, ions were also found at m/z 1488 and 744. The high-mass ion was assigned to $[[Ru[CCPhC(CF_3)_2C(CN)_2](PPh_3)(C_5H_5)]_2]^+$, which shows significant fragmentation by loss of PPh_3 and $CCPhC(CF_3)_2C(CN)_2$. The ion at m/z 744 was assigned to $[Ru[CCPhC(CF_3)_2C(CN)_2](PPh_3)(C_5H_5)]^+$, which has the same formulation as the molecular ion of the allyl complex 14.[2] Fragments from the m/z 744 peak result from the loss of CN and CF_3. The remaining peaks in the spectra result from the usual fragmentation of $Ru(PPh_3)(\eta\text{-}C_5H_5)$, with breakdown and loss of the phosphine groups and the cyclopentadienyl ligand.



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In solution, the nitrile compounds show intense colors that range from red (**8**) through yellow (**4**) to dark blue (**6**). The electronic absorption spectra for complexes containing the $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$ chromophore have common features. Strong peaks are present at around 234 nm (with shoulders at 286 and 336 nm, not resolved in all cases), which have been ascribed to intraligand transitions associated with the $Ru(PPh_3)(\eta\text{-}C_5H_5)$ core. For complexes with electron-deficient nitrile ligands containing unsaturated substituents, two charge-transfer absorptions were observed in the range 400–1000 nm. These are presumably MLCT transitions, Ru(II) → nitrile ($d\pi \rightarrow p\pi^*$). The two CT bands observed for each binuclear complex were found at lower energy (30–80 nm) than those of the related mononuclear complexes. This is in accordance with results obtained for the luminescent complexes $[[RuL_2]_m(ddp)]$ (L = phen, bpy; m = 1, 2; dpp = 2,3-bis(2-pyridyl)pyrazine].[5] In these, the Ru(II) → dpp transition is shifted to lower energy (71 nm) when the ligand is bridging, as a result of stabilization of the π^*-acceptor orbital on dpp.

Lower energy shifts in the CT bands were found for the most electron-deficient nitriles (546, 644 nm (**6**); 484, 534 nm (**8**); 470, 510 nm (**11**)). The position of the CT bands for the binuclear compounds also reflected the nature of the ligand (tcne 646, >900 nm (**13a**) > dcfe 560, 770 nm (**2a**) > tetrafluoroterephthalonitrile 562, 586 nm > tetrafluorophthalonitrile 506, 552 nm (**12**) ≈ fumaronitrile 492, 548 nm (**10b**)). This pattern could not be related directly to donor strengths, but the observed lowering in energy of the nitrile π^*-acceptor orbitals (hence lower energy absorption) with the more electron-withdrawing groups is as expected. The maxima of the first CT absorption for the isomers of 13 were found between 634 and 646 nm, while the second absorption had maxima greater than 900 nm.

All the reactions of the nitriles with 4 were performed with ca. 1/1 stoichiometry. In cases where binuclear complexes were formed, the same products were obtained when an excess of reactant 4 was used, but the reactions did not go to completion. The nitriles were chosen to evaluate the effects of (a) increasing the number of the nitrile sites available, (b) changing the steric requirements at the sites, and (c) varying the electronic properties of the nitrile. Examples of structurally characterized $RuX(PPh_3)_2(\eta\text{-}C_5H_5)$ complexes ($X = C(CN)_3$, $C(CN)_2C(CN)C(CN)_2$) containing N-bound tricyanomethanide and pentacyanopropenide anions have been described.[6,7] Related manganese complexes $[Mn(CO)_2(\eta\text{-}C_5H_4Me)]_nX$ (n = 1–4; X = tcne, terephthalonitrile, tetrafluoroterephthalonitrile), which contain bridging or terminal nitrile ligands, have also been obtained.[8]

A binuclear complex was formed from tetrafluoroterephthalonitrile, whereas the product obtained with terephthalonitrile was a mononuclear derivative. The difference in reactivity was related to tetrafluorophthalonitrile being a stronger π-acceptor ligand. Previous work had led to the synthesis of several cationic mononuclear derivatives of $[Ru(L)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ (L = MeCN, $CH_2{=}CHCN$, $o\text{-}C_6H_4(CN)_2$, $o\text{-}C_6F_4(CN)_2$) as well as to the bridged binuclear compounds $[[Ru(PPh_3)_2(\eta\text{-}C_5H_5)]_2L]^{2+}$ (L = $p\text{-}C_6F_4(CN)_2$, $m\text{-}C_6H_4(CN)_2$, $NC(CH_2)CN$).[9] Formation of

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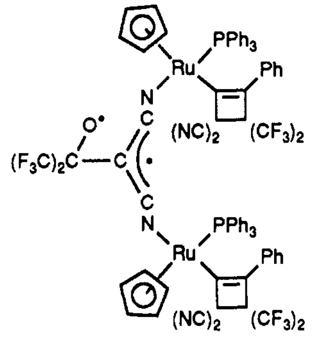
the binuclear complexes was favored when the nitrile groups were in a near-linear arrangement, which minimized interactions between the bulky PPh_3 groups on the two metal centers.

The synthesis of 4 works successfully because the small acetonitrile ligand readily replaces one of the bulky triphenylphosphine ligands. Molecular modeling has shown that there are mutual interactions between the two triphenylphosphine ligands, as well as with the cyclobutenyl phenyl substituent and the CF_3 groups. However, a similar loss of the phosphorus ligand is not a feature of the chemistry of the related complexes $RuX(PR_3)_2(\eta\text{-}C_5H_5)$ (R = Me, OMe; X = Cl, C_2Ph, $C{=}CPh(CN)_2C(CN)_2$).[1,10] This is to be expected, as the cone angles of these *P*-donor ligands (PMe_3, 118°; $P(OMe)_3$, 107°) are considerably smaller than that of PPh_3 (145°).

Two green complexes were also discovered in the reactions of 4 with dcfe; these are thought to be isomers of the oxygen adduct $[Ru[C{=}CPhC(CF_3)_2C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)]_2[\mu\text{-}(NC)_2CC(CF_3)_2O]$ (**15a,b**), formed by oxidation of **2a** and **2b**, respectively. The analytical and FAB mass spectrometric results confirm the dimeric structure of **15b**; **15a** has properties similar to those of **15b**, but reproducible analyses were not obtained. In the IR spectra of **15a** and **15b**, the ν(CN) region contained a two-band pattern. The upper band is at higher frequency than the corresponding bands in either **2a** or **2b**. As these strong ν(CN) bands can be assigned to the *N*-bound nitrile, it is clear that the oxidation has taken place at the bridging group. No absorptions assignable to ν(OH) were found in the IR spectra of the two isomers of 15. These compounds had fingerprint regions similar to those of **2a** and **2b**, but the ν(C=C) bands were less intense. Protonated molecular ions were found in the FAB mass spectra at *m/z* 1720 for **15a** and **15b**, the fragmentation patterns being similar to those of the other binuclear complexes mentioned previously. The proton NMR spectra of **15a** and **15b** were nearly featureless, with only very weak, broad resonances being found in the phenyl region. The reduction process observed for the dcfe ligand (see below) in complexes **2a** and **2b** was completely absent in **15b**. It seems likely that this reduction process is associated with the LUMO localized on the ligand, which in turn suggests that the LUMO on the bridging group has been either raised in energy or changed in character altogether in the transformation from 2 to 15. From these results it appears that addition of "O" to the bridging group in 2 has removed the π-system and formed a radical, this having an oxidation potential outside the solvent window. A structure involving an epoxide diradical group is consistent with these observations. The ready oxidation of free cyanoolefins, e.g., tcne, to epoxides by H_2O_2 has been described.[11]



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The ESR spectra of **2a,b** and both isomers of 15 all show the same broad signal (31 G peak-to-peak line width) at $g = 2.038$. This was investigated further and found to be the result of small amounts of the isomers of 15 being present in solutions of **2a** or **2b**, even after chromatography. Partial conversion of **2a** to **15a** and of **2b** to **15b** took place over 4 days in benzene solutions under O_2. The conversion of **2a** to **15a** (major amount) and **15b** (minor amount) was also facilitated by supporting the complex on silica. A possibility that a catalytic route may be involved in the syntheses of **15a** and **15b** is supported by the increased conversion of **2a** to **15a** and **15b** on silica. These results suggest that the paramagnetic species are the two isomers of 15. Small amounts of these isomers are always present in solutions of **2a**, explaining the anomalously low value of unpaired electrons observed in the first preparations of **2a**.

Electrochemistry. It was decided to undertake an electrochemical study of the nitrile complexes to see if the number of couples observed and their $E_{1/2}$ values could be used to determine whether the complexes formed were mononuclear or binuclear. Recent investigations[12,13] have shown that the redox chemistry of the compounds $Ru(R)(L)_2(\eta\text{-}C_5R'_5)$ (where R = C_2Ph, C_2Bu^t, Me, CH_2Ph, Cl; L = CO, PPh_3; L_2 = dppe; R′ = H, Me) is characterized by the one-electron-oxidation process Ru(II) → Ru(III). For the C_5H_5 complexes, this process is quasi-reversible and occurs at around 0.5 V. Our results for $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (1) agree well with those reported earlier,[12] which are for a quasi-reversible process occuring at $E_{1/2} = 0.60$ V (0.56 V corrected for the $FeCp_2/FeCp_2^+$ couple). We also looked at the oxidation process observed for $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$, which had a $E_{1/2} = 0.74$ V, and found that this was near-reversible but was not diffusion-controlled.

The electrochemical results are summarized in Table III. The cyclobutenyl and nitrile ligands shift the Ru(II) → Ru(III) couple to 0.89 V for 4 and 0.87 V for 5. Higher oxidation potentials were observed when the more deficient nitrile ligands were present: $E_{1/2}$ = 1.07 (6), 0.95 (7), 1.07 (11), 1.05 (8), and 0.97 (9). The chemical reversibility of the processes in 4 and 11 suggests that it might be possible to modify the environment of the ruthenium with substituents other than C_5Me_5 to obtain relatively stable 17-electron Ru(III) radical cations. Related 17-electron Fe(III) cations have been characterized for several $FeR(L)_2(\eta\text{-}C_5H_5)$ complexes (L = CO, PPh_3; L_2 = dppe; R = Cl, Br, H, Me),[14,15] but not for the ruthenium analogues investigated.[13] The oxidation processes observed for the other mononuclear compounds were either quasi- or near-reversible and, in some instances, were diffusion-controlled (6, 7, and 11).[16]

With use of square-wave voltammetry, two oxidation processes were measured in the binuclear complexes, confirming their stoichiometry. As an example, the cyclic voltammogram of complex **2a** is shown in Figure 3. The

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Table III. Electrochemical Data for the Nitrile Complexes[a]

	compd							
	4	**5**	**6**	**7**	**11**	**8**	**9**	**12**
Square-Wave Voltammetry								
1st oxidn E_p	0.81	0.84	1.06	0.95	1.00	1.03	0.96	1.04
2nd oxidn E_p								1.10
1st redn E_p			−0.58	−1.59	−1.34	−0.97	−1.20	−1.24
2nd redn E_p			−1.61					
Cyclic Voltammetry								
1st oxidn process								
$E_{1/2}$	0.89	0.87	1.07	0.95	1.07	1.05	0.97	1.08
E_{pa}	1.26	0.96	1.13	1.02	1.31	1.16	1.07	1.18
E_{pc}	0.51	0.78	1.01	0.89	0.83	0.93	0.88	0.97
n_{rel}			1	1	1	1	1	2
reversibility	rev	q-rev	n-rev	q-rev	rev	q-rev	q-rev	q-rev
diffusion control	no	no	yes	yes	yes	no	no	no
1st redn process								
$E_{1/2}$			−0.55			−0.97		
E_{pa}			−0.49			−0.85		
E_{pc}			−0.60	−1.66	−1.56	−1.09	−1.28	−1.50
n_{meas}*, n_{rel}			1*	~1	2	1	1	2
reversibility			rev	irrev	irrev	rev	irrev	irrev
diffusion control			yes	yes	no	no	no	no
2nd redn process								
E_{pc}			−1.64					
n_{rel}			~2					
reversibility			irrev					
rest E			−0.56	−0.93			−1.08	−1.03

	compd							
	10a	**10b**	**13a**	**13b**	**13c**	**2a**	**2b**	**15b**
Square-Wave Voltammetry								
1st oxidn E_p	0.92	0.94	−0.10	−0.11	−0.03	0.14	0.10	0.07
2nd oxidn E_p	1.06	1.07	1.11	1.12	1.00	0.66	0.64	0.63
1st redn E_p	−1.20	−1.20	−1.03	−1.05	−1.06	−0.46	−0.47	
Cyclic Voltammetry								
1st oxidn process								
$E_{1/2}$	0.95	0.93	−0.08	−0.09	−0.06	0.13	0.10	0.10
E_{pa}	1.04	0.99	−0.02	−0.01	0.03	0.17	0.17	0.19
E_{pc}	0.86	0.88	−0.14	−0.17	−0.09	0.10	0.02	−0.01
n_{rel}	1	1	1	1	1	1	1	1
reversibility	q-rev	q-rev	q-rev	q-rev	n-rev	rev	rev	rev
diffusion control	yes	yes	no	no	no	no	no	no
2nd oxidn process								
$E_{1/2}$	1.09	1.07	1.12	1.16	1.02	0.67	0.67	0.66
E_{pa}	1.12	1.09	1.17	1.24	1.07	0.72	0.74	0.76
E_{pc}	1.05	1.05	1.07	1.09	0.97	0.61	0.59	0.56
n_{rel}	1	1	1	1	1	1	1	1
reversibility	q-rev	q-rev	rev	rev	q-rev	rev	rev	rev
diffusion control	yes	yes	no	no	no	no	no	no
1st redn process								
$E_{1/2}$	−1.19		−0.85	−1.00	−0.88	−0.45	−0.46	
E_{pa}	−1.08		−0.60	−0.80	−0.58	−0.40	−0.37	
E_{pc}	−1.30	−1.27	−1.10	−1.19	−1.17	−0.50	−0.55	
n_{rel}	1	1	1	1	1	1	1	
reversibility	q-rev	irrev	q-rev	q-rev	q-rev	q-rev	q-rev	
diffusion control	no	no	no	no	no	no	no	
rest E	−1.08				−0.04	−0.18		0.03

[a] All E values are in volts.

cyclic voltammetry results for **12** did not resolve the two processes, which appeared as one two-electron process. Most of these processes were quasi-reversible, although those of **2a**, **2b**, and **14b** were fully reversible. The oxidation potentials for **14b** ($E_{1/2}$ = 0.10, 0.66 V) were in good agreement with those found for the isomers of **2** ($E_{1/2}$ = 0.13, 0.67 V (**2a**), 0.10, 0.67 V (**2b**)), confirming a related binuclear structure for **14b**.

Reduction processes associated with the nitrile ligand were found for **6**–**9** and **11**. In general, the reduction of the coordinated ligand took place at potentials more negative than that observed for the free ligand. For **6** and **8**, the reduction processes were chemically reversible. In contrast, those of the free ligands were quasi-reversible. It appears that the metal stabilizes the radical anion associated with the nitrile ligand by charge delocalization. The other mononuclear complexes showed irreversible behavior for the reduction process. A comparison of CV and SW voltammetric currents for the first reduction of **6** with those of the oxidation of ferrocene under stirred conditions[13] suggested that this was a one-electron process. The diffusion coefficient for **6** appears to be only slightly smaller than that of ferrocene ($i_p \propto D^{1/2}$), which is somewhat unexpected. Comparison of the Ru(II) → Ru(III) oxidation[13] with the first reduction process helps to confirm that the reduction involves a one-electron transfer.

For the binuclear compounds other than **12**, the ratio of the number of electrons involved in the reduction to

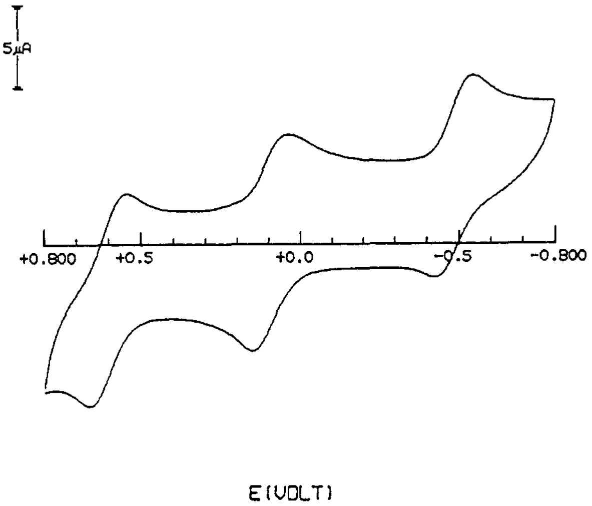

Figure 3. Cyclic voltammogram of **2a** (200 mV s^{-1}) in CH_2Cl_2.

those involved in the two oxidation processes was 1/1/1. For **12**, the ratio was 1/2. The reduction processes observed for **2a**, **10**, **12**, and **13** were either quasi-reversible or irreversible and took place at the same or at slightly more negative potentials than those of the free ligands. Little difference was found between the oxidation and reduction potentials of related mononuclear and binuclear complexes, the variations being within the scale of experimental error.

Conclusions

An acetonitrile–cyclobutenyl complex (**4**) was formed by treating the bis(triphenylphosphine) complex **3** with acetonitrile. This reaction is probably driven by the replacement of the bulky PPh_3 with the smaller MeCN ligand. Subsequent displacement of the acetonitrile ligand in **4** by other nitriles has allowed a number of mononuclear and binuclear nitrile-substituted cyclobutenyl complexes to be synthesized. The reaction of **4** with dcfe gave the binuclear complex **2a**, which had been synthesized earlier from $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ and dcfe in benzene. Complex **2a** thus prepared is weakly paramagnetic, even though an X-ray structure determination suggested otherwise. We have found that small amounts of the paramagnetic species **15a** and **15b**, formed by the oxidation of **2a** and suggested to have an epoxy radical formulation, were invariably present in solutions of **2a**.

Electrochemical studies were carried out on each of the nitrile complexes to determine whether they were mononuclear or binuclear. The presence of two metal-centered oxidation processes confirmed the formulation of the binuclear complexes, while the presence of one only indicated that the complex was mononuclear. For the complexes containing the nitriles MeCN, dcfe, and $o\text{-}C_6F_4(CN)_2$, the oxidation processes were reversible, which implies that it might be possible to isolate stable 17-electron species by modifying the ligands attached to the ruthenium.

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. Solvents used were dried and distilled under nitrogen. Petroleum ether was a fraction with bp 62–66 °C. Melting points were measured in sealed capillaries with a Gallenkamp melting point apparatus and are uncorrected. Thin-layer chromatography (TLC) was performed on 20 × 20 cm glass plates with a 0.5 mm thick silica adsorbent (60 GF_{254}, Merck). Microanalyses were performed by the Canadian Microanalytical Service, New Westminster, British Columbia, Canada. Electron microprobe analyses were by the Electron Optical Centre, University of Adelaide.

Instrumentation. IR Spectra. Perkin-Elmer 683 double-beam and Perkin-Elmer 1720X FT spectrometers, with NaCl optics, were calibrated by using the polystyrene absorption at 1601.4 cm^{-1}.

Electronic Spectra. Electronic spectra were recorded on a Hewlett-Packard 8452A diode array spectrometer, using a 1-cm quartz cell.

NMR Spectra. Bruker CXP 300 (^1H NMR at 300.13 MHz, ^{19}F NMR at 282.35 MHz, ^{31}P NMR at 121.49 MHz, ^{13}C NMR at 75.47 MHz) and Bruker WP 80 (^1H NMR at 80 MHz, ^{13}C NMR at 20.1 MHz) spectrometers were used, with the references $CFCl_3$ (^{19}F; internal) or 0.1 M HCl/0.01 M H_3PO_4 in D_2O (^{31}P; external, δ +0.8 ppm). The shifts quoted for the ^{31}P NMR spectra are relative to 85% H_3PO_4.

ESR Spectra. A Varian EPR E-9 spectrometer operating in the X-band was employed; dpph was used as a "g marker".

Mass Spectra. FAB mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon and xenon were used as FAB gases, with source pressures of typically 10^{-6} bar; the FAB gun voltage was 7.5 kV, with a current of 1 mA. The ion-accelerating potential was 7 kV. The complexes were made up as ca. 0.5 M solutions in CH_2Cl_2; 1 drop was added to 1 drop of matrix (3-nitrobenzyl alcohol), and the mixture was applied to the FAB probe tip. Spectra are reported below in the form *m/z*, assignment, relative intensity. EI MS spectra were obtained on a GEC-Kratos MS3074 mass spectrometer (70-eV ionizing energy, 4-kV accelerating potential).

Electrochemistry. Electrochemical analyses were performed by use of a BAS-100 electrochemical analyzer with a cell containing Pt-disk (Bioanalytical Systems) working, Pt-wire counter, and SCE reference electrodes. The reference electrode was separated from the cell by a bridge containing electrolyte, which was fitted with a fine glass frit. A 0.1 M solution of $[NBu_4][BF_4]$ in CH_2Cl_2 was used as the supporting electrolyte, and the concentration of compounds was approximately 2×10^{-4} M. Spectra were recorded at 25 °C, and all potentials are in volts relative to the SCE, at which E_p^{ox} for $FeCp_2$ was 0.60 V (differential pulse).

The CV peaks listed were recorded at a scan rate of 200 mV s^{-1}. The criterion for diffusion control was $i^p/v^{1/2}$ = constant, with variation of v between 50 and 500 mV s^{-1}. Criteria for reversibility were as follows: (given for an oxidation process): $i^{p,a}/i^{p,c} = 1.0$ reversible; $i^{p,a}/i^{p,c} < 1.2$, near-reversible; $i^{p,a} > i^{p,c}$, quasi-reversible; no apparent cathodic peak, irreversible. For a multiprocess CV scan, the ratio of the peak current for the process being measured to that of the process with the smallest peak current was expressed as an integer value, n_{rel}. The number of electrons, n_{meas}, involved in a square-wave (SW) process was determined by comparison with $FeCp_2/FeCp_2^+$ under stirred voltammetry conditions. Sqaure wave parameters were as follows: sweep width amplitude 25 mV, frequency 15 Hz, step E 4 mV; sweeps performed in a negative direction, +1.50 → −1.50 V. Differential pulse parameters were as follows: pulse amplitude 50 mV, pulse width 60 ms, pulse period 1000 ms; sweeps performed in a negative direction at 4 mV s^{-1}.

Starting Materials. Literature methods were used to prepare $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$[16] and $C(CN)_2{=}C(CF_3)_2$ (dcfe).[17] The other nitriles were commercial samples and were used as received; $Me_2NO{\cdot}2H_2O$ (Aldrich) was dehydrated by sublimation before use.

Syntheses. $Ru[C{=}CPhC(CF_3)_2C(CN)_2](NCMe)(PPh_3)(\eta\text{-}C_5H_5)$ (4). (a) To a suspension of $Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)$ (400 mg, 0.51 mmol) in MeCN (50 mL) was added dcfe (140 mg, 0.65 mmol). With vigorous stirring the suspension quickly dissolved, and after the mixture was cooled (to 0 °C), a yellow precipitate of $Ru[C{=}CPhC(CF_3)_2C(CN)_2](PPh_3)_2(\eta\text{-}C_5H_5)$ (**3**) formed. This was collected and washed with MeCN (3 × 5 mL). The precipitate was suspended in MeCN (80 mL) and the suspension stirred at room temperature for 1.5 days, giving a clear pale yellow solution. The solution was filtered and the volume reduced (HV; HV =

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[17] Middleton, W. J. *J. Org. Chem.* **1965**, *30*, 1402.

vacuum) until a yellow microcrystalline product formed. This was washed with EtOH and petroleum ether and dried under vacuum, giving Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](NCMe)(PPh$_3$)(η-C$_5$H$_5$) (**4**; 170 mg, 0.22 mmol, 43%), mp 154–155 °C. (The analytical sample was prepared by crystallization (CH$_2$Cl$_2$/petroleum ether) at -15 °C.) Anal. Calcd for C$_{39}$H$_{28}$F$_6$N$_3$PRu·0.75CH$_2$Cl$_2$: C, 56.27; H, 3.50; N, 4.95. Found: C, 56.33; H, 3.84; N, 4.88. FAB MS: 1529, [M$_2$ - MeCN]$^+$, 0.9; 785, M$^+$, 8; 744, [M - MeCN]$^+$, 36; 429, [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$, 100. UV (CH$_2$Cl$_2$): 234 (ϵ 43 000), 286 (7000), 336 nm (3000). IR (Nujol mull): ν(CN) 2267 (m), 2235 (w) cm^{-1}; ν(CC) 1613 (m), 1590 (w), 1576 (m) cm^{-1}; ν(CF)1310 (sh), 1293 (sh), 1281 (s, br), 1246 (sh), 1222 (s), 1200 (s), 1190 (sh), 1099 (s) cm^{-1}. Addition of EtOH to the combined filtrates followed by volume reduction gave a further yellow precipitate of **4** (162 mg, 0.21 mmol, 41%), which, after washing with EtOH and petroleum ether and drying, was suitable for further preparative chemistry but was not analytically pure.

(b) A solution of [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$)]$_2$[μ-(NC)$_2$C=C(CF$_3$)$_2$] (**2a**; 96 mg, 0.056 mmol) in MeCN (50 mL) was refluxed for 4 h, by which time the solution had changed from blue to yellow. The solvent was removed from the filtered solution under vacuum and the product crystallized twice (CH$_2$Cl$_2$/petroleum ether) to give large dark yellow crystals of Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](NCMe)(PPh$_3$)(η-C$_5$H$_5$) (**4**; 35 mg, 0.044 mmol, 40%).

Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](NCCH=CH$_2$)(PPh$_3$)(η-C$_5$H$_5$) (5). Acrylonitrile (24 mg, 0.46 mmol) was added to a solution of **4** (100 mg, 0.13 mmol) in benzene (20 mL). After the mixture was stirred for 15 h, the solvent was removed from the yellow solution under reduced pressure. The residue was chromatographed (TLC: CH$_2$Cl$_2$/petroleum ether 1/1), and a major yellow band (R_f 0.53) was collected and crystallized (CH$_2$Cl$_2$/MeOH) to give yellow crystalline Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](NCCH=CH$_2$)(PPh$_3$)(η-C$_5$H$_5$) (**5**; 68 mg, 0.087 mmol, 68%), mp 169–172 °C. Anal. Calcd for C$_{40}$H$_{28}$F$_6$N$_3$PRu: C, 60.30; H, 3.54; N, 5.28. Found: C, 59.73; H, 3.52; N, 5.23. FAB MS: 1541, [M$_2$ - CH$_2$CHCN]$^+$, 2; 797, M$^+$, 6; 744, [M - CH$_2$CHCN]$^+$, 29; 429, [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$, 100. UV (CH$_2$Cl$_2$): 234 (ϵ 40 000), 334 nm (11 000). IR (Nujol mull): ν(CN) 2240 (sh), 2223 (s) cm^{-1} ν(CC) 1614 (m), 1601 (sh), 1587 (w), 1574 (s) cm^{-1}; ν(CF) 1269 (s), 1200 (s), 1183 (sh), 1107 (s), 1096 (s), 1089 (sh) cm^{-1}. The other three minor/trace bands were not characterized.

Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$][(NC)C$_6$H$_2$(CN)$_3$](PPh$_3$)(η-C$_5$H$_5$) (6). 1,2,4,5-Tetracyanobenzene (19 mg, 0.11 mmol) was added to **4** (100 mg, 0.13 mmol) in benzene (20 mL). Stirring for 15 h resulted in a dark blue solution. The solvent was removed under reduced pressure and the residue separated by TLC (petroleum ether/CH$_2$Cl$_2$/acetone 6/2/1). A major blue band (R_f 0.57) was collected, and this product crystallized (CH$_2$Cl$_2$/hexane) as dark blue plates of Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$][(NC)C$_6$H$_2$(CN)$_3$](PPh$_3$)(η-C$_5$H$_5$) (**6**; 31 mg, 0.034 mmol, 26%), mp 265 °C dec. Anal. Calcd for C$_{47}$H$_{27}$F$_6$N$_6$PRu·0.5CH$_2$Cl$_2$: C, 59.17; H, 2.93; N, 8.72. Found: C, 59.76; H, 3.33; N, 8.52. FAB MS: 1666, [M$_2$ - C$_6$H$_2$(CN)$_4$]$^+$, 0.6; 922, M$^+$, 2; 744, [M - C$_6$H$_2$(CN)$_4$]$^+$, 18; 429, [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$, 100. UV (CH$_2$Cl$_2$): 232 (ϵ 47 000), 266 (26 000), 306 (13 000), 546 (9000), 644 nm (10 000). IR (Nujol mull): ν(CN) 2242 (w), 2180 (s) cm^{-1}; ν(CC) 1611 (w), 1596 (sh), 1587 (m), 1572 (sh) cm^{-1}; ν(CF) 1290 (sh), 1266 (s), 1237 (m), 1193 (s), 1097 (sh), 1088 (sh) cm^{-1}. A further major green band (R_f 0.7) was collected and tentatively characterized as [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$)]$_2$[μ-(NC)$_2$C$_6$H$_2$(CN)$_2$] (37 mg, 0.22 mmol, 35%). However, another compound (probably an isomer) ran with precisely the same R_f and could not be separated from the green compound, the proportions of the two compounds varying with the duration of the reaction. Spectroscopic data for the impure green complex is as follows. IR (Nujol): ν(CN) 2238 vw, 2171 s cm^{-1}; ν(CC) 1610 w, 1573 w cm^{-1}; ν(CF) 1290 (sh), 1270 s, 1220 (sh), 1201 s cm^{-1}; other peaks at 1480 m, 1436 m, 1109 m, 1094 m, 1071 w, 1027 w, 942 w, 832 w, 814 (sh), 807 w, 769 w, 747 m, 719 m, 704 (sh), 694 m, 630 w cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 7.2–6.6 (m, Ph + C$_6$H$_2$(CN)$_4$), 5.01 (d, J = 3.0 Hz, 4 H, C$_5$H$_5$), 4.51 (s, 1 H, C$_5$H$_5$, impurity). FAB MS (selected ions): 2410*, [M]$^+$, 1; 2096*, [M - C=CPhC(CF$_3$)$_2$C(CN)$_2$]$^+$, 0.1; 1666, [1488 + C$_6$H$_2$(CN)$_4$]$^+$, 0.5; 1488*, [[Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(C$_5$H$_5$)]$_2$]$^+$, 0.7; 1350, [1488 - C=CPhC(CF$_3$)$_2$C(CN)$_2$]$^+$, 0.5; 1226*, [1488 - PPh$_3$]$^+$, 0.3; 1173*, [1488 - C=CPhC(CF$_3$)$_2$C(CN)$_2$]$^+$, 0.5; 911*, [1173 - PPh$_3$]$^+$, 0.8; 744, [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(C$_5$H$_5$)]$^+$ 16; 429*, [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$, 100. The green fraction and **6** appeared to interconvert in solution (after further TLC). Three minor blue-purple bands were also collected. These were examined by FAB MS; two appeared to be isomers of [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$)]$_2$[μ-(NC)$_2$C$_6$H$_2$(CN)$_2$] ([M]$^+$ 1666, ratio of ions [M]$^+$/[Ru(PPh$_3$)(C$_5$H$_5$)]$^+$ >1%) and the third the hydration product Ru[C$_2$PhC(CN)$_2$C(CF$_3$)$_2$][C$_6$H$_2$(CN)$_4$·H$_2$O](PPh$_3$)(η-C$_5$H$_5$) ([M]$^+$ 940).

Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$][(NC)C$_6$H$_4$(CN)-*o*](PPh$_3$)(η-C$_5$H$_5$) (7). Phthalodinitrile (22 mg, 0.17 mmol) was added to a solution of **4** (100 mg, 0.13 mmol) in benzene (10 mL). The solution became orange over 16 h, after which time the solvent was removed under reduced pressure and the residue chromatographed (TLC: petroleum ether/acetone 2/1). A major orange band (R_f 0.73) was quickly removed and precipitated (CH$_2$Cl$_2$/pentane) as an orange powder of Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$][(NC)C$_6$H$_4$(CN)-*o*](PPh$_3$)(η-C$_5$H$_5$) (**7**; 35 mg, 0.04 mmol, 32%), mp 156–157 °C. Anal. Calcd for C$_{45}$H$_{29}$F$_6$N$_4$PRu: C, 62.00; H, 3.35: N, 6.43. Found: C, 62.38; H, 3.47; N, 6.31. FAB MS: 1616, [M$_2$ - C$_6$H$_4$(CN)$_2$]$^+$, 0.4; 872, M$^+$, 5; 744, [M - C$_6$H$_4$(CN)$_2$]$^+$, 17; 429, [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$, 100. UV (CH$_2$Cl$_2$): 234 (ϵ 51 000), 266 (19 000), 400 (8000), 448 nm (7000). IR (Nujol mull): ν(CN) 2244 (sh), 2240 (m) 2211 (s) cm^{-1}; ν(CC) 1612 (w), 1593 (m), 1571 (m) cm^{-1}; ν(CF) 1310 (sh), 1295 (sh), 1272 (s), 1223 (s), 1197 (s), 1008 (sh) cm^{-1}. This complex was somewhat unstable in solution and slow crystallization was unsuccessful.

Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$][(NC)C$_6$F$_4$(CN)-*o*](PPh$_3$)(η-C$_5$H$_5$) (11) and [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$)]$_2$[μ-(NC)$_2$C$_6$F$_4$-*o*] (12). Tetrafluorophthalodinitrile (33 mg, 0.17 mmol) was added to a solution of **4** (100 mg, 0.13 mmol) in benzene (10 mL). The resulting deep red solution was evaporated to dryness after 48 h and the products separated by TLC (petroleum spirit/CH$_2$Cl$_2$ 1/1). A magenta band (R_f 0.68) was collected and crystallized (CH$_2$Cl$_2$/hexane) to give dark purple crystals of [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$)]$_2$[μ-(NC)$_2$C$_6$F$_4$-*o*] (**12**; 18 mg, 0.011 mmol, 17%), mp 154–155 °C. Anal. Calcd for C$_{82}$H$_{50}$F$_{16}$N$_6$P$_2$Ru$_2$: C, 57.84; H, 3.44; N, 4.67. Found: C, 56.95; H, 3.30; N, 4.60. FAB MS: 1688, M$^+$, 2; 1373, [M - CCPhC(CF$_3$)$_2$C(CN)$_2$]$^+$ 2; 744, [Ru[CCPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(C$_5$H$_5$)]$^+$, 40; 429, [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$, 100. UV (CH$_2$Cl$_2$): 234 (ϵ 77 000), 276 (41 000), 342 (11 000), 506 (21 000), 552 nm (19 000). IR (Nujol mull): ν(CN) 2242 (vw), 2204 (sh), 2195 (s) cm^{-1}; ν(CC) 1612 (vw), 1577 (vw) cm^{-1}; ν(CF) 1293 (sh), 1273 (s), 1204 (s) cm^{-1}. The next major red band (R_f 0.35) was removed quickly and precipitated (CH$_2$Cl$_2$/pentane) as a dark red powder of Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$][(NC)C$_6$F$_4$(CN)-*o*](PPh$_3$)(η-C$_5$H$_5$) (**11**; 73 mg, 0.077 mmol, 61%), mp 146–148 °C. Anal. Calcd for C$_{45}$H$_{25}$F$_{10}$N$_4$PRu: C, 57.27; H, 2.67; N, 5.94. Found: C, 56.93; H, 2.66; N, 6.29. FAB MS: 1688, [M$_2$ - C$_6$F$_4$(CN)$_2$]$^+$ 0.4; 944, M$^+$, 5; 744, [M - C$_6$F$_4$(CN)$_2$]$^+$, 49; 429, [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$, 100. UV (CH$_2$Cl$_2$): 234 (ϵ 44 000), 258 (28 000), 282 (21 000), 344 (5000), 470 (10 000), 510 nm (12 000). IR (Nujol mull): ν(CN) 2239 (vw), 2193 (s) cm^{-1}; ν(CC) 1612 (w), 1577 (w) cm^{-1}; ν(CF) 1290 (sh), 1272 (s), 1250 (sh), 1202 (s) cm^{-1}. Two other trace green bands were not collected. The two compounds **11** and **12** appeared to interconvert in solution; in the case of **11** this precluded slow crystallization.

Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$][(NC)C$_6$F$_4$(CN)-*p*](PPh$_3$)(η-C$_5$H$_5$) (8). A mixture of tetrafluoroterephthalodinitrile (40 mg, 0.20 mmol) and **4** (100 mg, 0.13 mmol) in benzene (20 mL) was stirred for 16 h, resulting in a deep red solution. The solvent was removed and the residue purified by TLC (cyclohexane/Et$_2$O/CH$_2$Cl$_2$ 6/2/1). A major burgundy band (R_f 0.5) was quickly removed and precipitated (CH$_2$Cl$_2$/petroleum ether) as a dark red powder of Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$][(NC)C$_6$F$_4$(CN)-*p*](PPh$_3$)(η-C$_5$H$_5$) (**8**; 68 mg, 0.072 mmol, 57%),mp 185–187 °C. Anal. Calcd for C$_{45}$H$_{25}$F$_{10}$N$_4$PRu: C, 57.27; H, 2.67; N, 5.94. Found: C, 56.67; H, 2.67; N, 6.12. FAB MS: 1688, [M$_2$ - C$_6$F$_4$(CN)$_2$]$^+$, 0.6; 944, M$^+$, 2; 744, [M - C$_6$F$_4$(CN)$_2$]$^+$ 25; 429 [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$, 100. UV (CH$_2$Cl$_2$): 238 (ϵ 44 000), 256 (34 000), 290 (14 000), 484 (12 000), 534 nm (13 000). IR (Nujol mull): ν(CN) 2249 (w), 2199 (sh), 2179 (s) cm^{-1}; ν(CC) 1644 (m), 1610 (w), 1569 (w) cm^{-1}; ν(CF) 1290 (sh), 1269 (s), 1219 (s), 1200 (s), 1182 (sh) cm^{-1}. This product was separated from a minor purple band (R_f 0.6), which had a tendency to crystallize on TLC plates. Apparent interconversion in solution was observed between 8 and this purple complex. The purple compound, which appears to be [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$)]$_2$[μ-(NC)$_2$C$_6$F$_4$-*p*], could not be purified effectively for analysis. Spectroscopic data for this complex are as follows. IR (Nujol): ν(CN) 2242 vw, 2192 s cm^{-1}; ν(CC) 1692 w (br), 1650 w (br), 1611 w, 1572 w cm^{-1}; ν(CF) 1288 (sh), 1273 s, 1201 s cm^{-1}; other peaks at 1497 m, 1439 m, 1400 w, 1322 w, 1219 w, 1165 w, 1109 (sh), 1098 m, 987 w, 943 w, 869 w, 836 w, 807 w, 748 w, 719 w, 705 (sh), 697 m, 641 w cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.3–6.4 (m, 40 H, Ph), 4.66 (d, J_{PH} = 3.1 Hz, 10 H, C$_5$H$_5$). ^{19}F NMR (CDCl$_3$): δ –66.1 (q, J_{FF} = 9 Hz, 6 F, CF$_3$), –66.4 (q, j_{FF} = 9 Hz, 6 F, CF$_3$), –132.7 (d, J_{FF} = 14 Hz, 4 F, F-*o*). FAB MS (selected ions): 1688,, [M]$^+$, 1; 1488, [[Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(C$_5$H$_5$)]$_2$]$^+$, 0.8; 1173, [1488 – C=CPhC(CF$_3$)$_2$C(CN)$_2$]$^+$, 0.9; 911, [1173 – PPh$_3$]$^+$, 2; 744, [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(C$_5$H$_5$)]$^+$, 31; 667*, [744 – Ph]$^+$, 6; 429*, [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$, 100; 362*, [Ru(PPh$_3$)]$^+$, 15; 352*, [Ru(PPh$_2$)(C$_5$H$_5$)]$^+$, 25; 244*, [RuPh(C$_5$H$_5$)]$^+$ 17. UV (CH$_2$Cl$_2$): 586 (ϵ* 2.2), 562 (2.1), 256 (4.8), 232 (7.6) nm; ϵ* values are relative values.

Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$][*trans*-(NC)CH=CH(CN)](PPh$_3$)(η-C$_5$H$_5$) (9) and Two Isomers of [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$)]$_2$[μ-*trans*-(NC)HC=CH(CN)] (10a,b). Fumaronitrile (11 mg, 0.14 mmol) was added to a solution of **4** (100 mg, 0.13 mmol) in benzene (15 mL). A ruby red solution developed over 16 h, after which time the solvent was removed and the residue separated by TLC (petroleum ether/CH$_2$Cl$_2$ 1/1). Three major bands were collected and crystallized (CH$_2$Cl$_2$/petroleum ether): the first purple band (R_f 0.78) was identified as [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$)]$_2$[μ-*trans*-(NC)HC=CH(CN)] (**10a**; 20 mg, 0.013 mmol, 20%), mp 178–179 °C, the next purple band (R_f 0.72) as [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$)]$_2$[μ-*trans*-(CN)HC=CH(CN)] (**10b**; 25 mg, 0.016 mmol, 25%), mp 187–189 °C, and the third orange band (R_f 0.34) as Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$][*trans*-(NC)CH=CH(CN)](PPh$_3$)(η-C$_5$H$_5$) (**9**; 41 mg, 0.060 mmol, 39%), mp 174–176 °C. The analytical and spectroscopic data for **10a** are as follows. Anal. Calcd for C$_{78}$H$_{52}$F$_{12}$N$_6$P$_2$Ru$_2$·CH$_2$Cl$_2$: C, 57.62; H, 3.39; N, 5.08. Found: C, 57.50; H, 3.30; N, 5.09. FAB MS: 1566, M$^+$, 2; 1251, [M – CCPhC(CF$_3$)$_2$C(CN)$_2$]$^+$, 0.6; 744, [Ru[CCPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(C$_5$H$_5$)]$^+$, 25; 429, [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$, 100. UV (CH$_2$Cl$_2$): 234 (ϵ 69 000), 256 (23 000), 502 (21 000), 564 nm (24 000). IR (Nujol mull); ν(CN) 2240 (w), 2200 (s) cm^{-1}; ν(CC) 1610 (w), 1580 (w) 1564 (w) cm^{-1}; ν(CF) 1268 (s), 1220 (m), 1198 (s), 1184 (sh) cm^{-1}. Analytical and spectroscopic data for **10b** are as follows. Anal. Calcd for C$_{78}$H$_{52}$F$_{12}$N$_6$P$_2$Ru$_2$·1.5CH$_2$Cl$_2$: C, 56.40; H, 3.33; N, 4.96. Found: C, 56.62; H, 3.39; N, 4.95. FAB MS: 1566, M$^+$, 1; 1251, [M – CCPhC(CF$_3$)$_2$C(CN)$_2$]$^+$, 0.6; 744, [Ru[CCPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(C$_5$H$_5$)]$^+$, 31; 429, [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$, 100. UV (CH$_2$Cl$_2$): 234 (ϵ 80 000), 256 (45 000), 290 (26 000), 492 (24 000), 548 nm (27 000). IR (Nujol mull): ν(CN) 2239 (w), 2202 (s) cm^{-1}; ν(CC) 1610 (w), 1575 (w) cm^{-1}; ν(CF) 1291 (sh), 1268 (s), 1219 (m), 1198 (s), 1181 (sh) cm^{-1}. Analytical and spectroscopic data for **9** are as follows. Anal. Calcd for C$_{41}$H$_{27}$F$_6$N$_4$PRu: C, 59.93; H, 3.31; N, 6.82. Found: C, 59.64; H, 3.38; N, 6.70. FAB MS: 1566, [M$_2$ – C$_2$H$_2$(CN)$_2$]$^+$, 0.7; 822, M$^+$, 2; 744, [M – C$_2$H$_2$(CN)$_2$]$^+$, 24; 429, [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$, 100. UV (CH$_2$Cl$_2$): 234 (ϵ 39 000), 256 (23 000), 292 (10 000), 444 (11 000), 498 nm (8000). IR (Nujol mull): ν(CN) 2236 (vw), 2226 (vw), 2186 (s), 2179 (s) cm^{-1}; ν(CC) 1611 (w), 1597 (sh), 1570 (w) cm^{-1}; ν(CF) 1270 (s), 1219 (m), 1198 (s) cm^{-1}.

Three Isomers of [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$)]$_2$[μ-(NC)$_2$C=C(CN)$_2$] (13a–c). A solution of **4** (100 mg, 0.13 mmol) and tcne (7 mg, 0.055 mmol) in benzene (15 mL) was stirred for 16 h. Removal of the solvent from the blue solution followed by TLC (petroleum ether/acetone/CH$_2$Cl$_2$ 6/2/1) of the residue separated two blue bands and a green band from a complex mixture of products that remained near the base line. The first blue band (R_f 0.70) crystallized (CH$_2$Cl$_2$/cyclohexane) as light blue needles of [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$)]$_2$[μ-(NC)$_2$C=C(CN)$_2$] (**13a**; 10 mg 0.0062 mmol, 10%), mp 300 °C dec, the next band (R_f 0.67) crystallized (CH$_2$Cl$_2$/pentane) as light blue plates of [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$)]$_2$[μ-(NC)$_2$C=C(CN)$_2$] (**13b**; 13 mg, 0.008 mmol, 13%), mp 260 °C dec, and the green band (R_f 0.63) crystallized (CH$_2$Cl$_2$/pentane) as green plates of [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$)]$_2$[μ-(NC)$_2$C=C(CN)$_2$] (**13c**; 25 mg, 0.015 mmol, 24%), mp 265 °C dec. To avoid interconversion, recrystallizations of all three compounds were performed quickly. Analytical and spectrocopic data for **13a** are as follows. Anal. Calcd for C$_{80}$H$_{50}$F$_{12}$N$_8$P$_2$Ru$_2$: C, 59.48, H, 3.12; N, 6.94. Found: C, 60.09; H, 3.45; N, 6.72. FAB MS: 1616, M$^+$, 6; 1301, [M – CCPhC(CF$_3$)$_2$C(CN)$_2$]$^+$, 1; 744, [Ru[CCPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(C$_5$H$_5$)]$^+$, 20; 429, [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$, 100. UV (CH$_2$Cl$_2$): 232 (ϵ 70 000), 288 (34 000), 328 (14 000), 646 (19 000), >900 nm. IR (Nujol mull): ν(CN) 2289 (vw), 2206 (w), 2159 (s), 2095 (s), 2018 (sh) cm^{-1}; ν(CC) 1612 (m), 1585 (sh), 1572 (m) cm^{-1}; ν(CF) 1298 (sh), 1270 (s), 1220 (sh), 1200 (s), 1197 (sh) cm^{-1}. Analytical and spectroscopic data for **13b** are as follows. Anal. Calcd for C$_{80}$H$_{50}$F$_{12}$N$_8$P$_2$Ru$_2$·0.5CH$_2$Cl$_2$: C, 58.32; H, 3.10; N, 6.76. Found: C, 58.61; H, 3.26; N, 6.69. FAB MS: 1616, M$^+$, 3; 1301, [M – CCPhC(CF$_3$)$_2$C(CN)$_2$]$^+$, 0.6; 744, [Ru[CCPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(C$_5$H$_5$)]$^+$, 13; 429, [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$, 100. UV (CH$_2$Cl$_2$): 232 (ϵ 70 000), 292 (30 000), 640 (16 000), >900 nm. IR (Nujol mull): ν(CN) 2283 (vw), 2209 (w), 2158 (s), 2093 (s) cm^{-1}; ν(CC) 1610 (m), 1587 (sh), 1572 (m) cm^{-1}; ν(CF) 1290 (sh), 1270 (s), 1219 (sh), 1200 (s), 1186 (sh) cm^{-1}. Analytical and spectroscopic data for **13c** are as follows. Anal. Calcd for C$_{80}$H$_{50}$F$_{12}$N$_8$P$_2$Ru$_2$: C, 59.48; H, 31.2; N, 6.94. Found: C, 59.60; H, 3.22; N, 6.83. FAB MS: 1616, M$^+$, 1; 1301, [M – CCPhC(CF$_3$)$_2$C(CN)$_2$]$^+$, 0.4; 744, [Ru[CCPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(C$_5$H$_5$)]$^+$, 8; 429, [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$, 100. UV (CH$_2$Cl$_2$): 234 (ϵ 80 000), 308 (24 000), 634 (20 000), >900 nm. IR (Nujol mull): ν(CN) 2280 (vw), 2220 (vw), 2116 (vs) cm^{-1}; ν(CC) 1612 (w), 1572 (w) cm^{-1}; ν(CF) 1290 (s), 1270 (s), 1218 (sh), 1201 (s), 1187 (sh) cm^{-1}.

Two Isomers of [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$)]$_2$[μ-(NC)$_2$C=C(CF$_3$)$_2$] (2a,b) and Two Isomers of [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$)]$_2$[μ-(NC)$_2$C=C(CF$_3$)$_2$O] (15a,b). (a) The olefin dcfe (75 mg, 0.35 mmol) was added to a benzene (10 mL) solution of Ru(C$_2$Ph)(PPh$_3$)$_2$(η-C$_5$H$_5$) (225 mg, 0.28 mmol). The color changed from yellow to blue over a period of 4 h; after 15 h more Ru(C$_2$Ph)(PPh$_3$)$_2$(η-C$_5$H$_5$) (20 mg, 0.025 mmol) was added and the solution stirred for 1 h before removal of the solvent (HV). The residue was separated by TLC (CH$_2$Cl$_2$/petroleum ether 2/3). The first white band (R_f 0.85) was identified as PPh$_3$ (FAB MS, spot TLC). A second, purple band (R_f 0.70) was crystallized (CH$_2$Cl$_2$/petroleum ether, analysis; benzene/octane, unit cell) as dark purple crystalline [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$)]$_2$[μ-(NC)$_2$C=C(CF$_3$)$_2$] (**2a**; 45 mg, 0.026 mmol, 19%), mp 179–182 °C; the unit cell dimensions compared well with those obtained for the X-ray sample, which was weakly paramagnetic. Anal. Calcd for C$_{80}$H$_{50}$F$_{18}$N$_6$P$_2$Ru$_2$: C, 56.48; H, 2.96; N, 4.94. Found: C, 55.24; H, 3.09; N, 4.72. FAB MS: 1720, [M + O]$^+$, 1; 1488, [M – C$_2$(CF$_3$)$_2$(CN)$_2$]$^+$, 0.4; 1387, [M – CCPhC(CF$_3$)$_2$C(CN)$_2$]$^+$, 0.4; 744, [Ru[CCPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(C$_5$H$_5$)]$^+$, 20; 429, [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$, 100. UV (CH$_2$Cl$_2$): 232 (ϵ 74 000), 294 (29 000), 326 (10 000), 560 (12 000), 770 nm (17 000). IR (Nujol mull): ν(CN) 2239 (vw), 2178 (sh), 2151 (sh), 2112 (s), 2018 (m) cm^{-1}; ν(CC) 1613 (w), 1576 (w) cm^{-1}; ν(CF) 1308 (sh), 1291 (sh), 1270 (s), 1238 (s), 1219 (m), 1198 (s), 1187 (sh) cm^{-1}. The next blue band (R_f 0.65) crystallized (CH$_2$Cl$_2$/petroleum ether) as blue microcrystalline [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$)]$_2$[μ-(NC)$_2$C=C(CF$_3$)$_2$] (**2b**; 24 mg, 0.014 mmol, 10%), mp 110–112 °C. Anal. Calcd for C$_{80}$H$_{50}$F$_{18}$N$_6$P$_2$Ru$_2$: C, 56.48; H, 2.96; N, 4.94. Found: C, 56.98; H, 3.55; N, 4.69. FAB MS: 1720, [M + O]$^+$, 1; 1703, [M + H]$^+$, 2; 1488 [M – C$_2$(CF$_3$)$_2$(CN)$_2$]$^+$, 0.4; 1387, [M – CCPhC(CF$_3$)$_2$C(CN)$_2$]$^+$, 0.4; 744, [Ru[CCPhC(CF$_3$)$_2$C(CN)$_2$]]$^+$, 20; 429, [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$, 100. UV (CH$_2$Cl$_2$): 232 (ϵ 74 000), 240 (55 000), 324 (14 000), 572 (9000), 814 nm (16 000). IR (Nujol mull): ν(CN) 2241 (vw), 2175 (sh), 2150 (sh), 2117 (s), 2020 (s) cm^{-1}; ν(CC) 1622 (w), 1574 (w) cm^{-1}; ν(CF) 1272 (s), 1244 (s), 1205 (s) cm^{-1}. A minor green band (R_f 0.35) crystallized (CH$_2$Cl$_2$/octane) as dark green crystals of [Ru[C=CPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$)]$_2$[μ-(NC)$_2$C=C(CF$_3$)$_2$O] (**15b**; 13 mg, 0.0075 mmol, 5%), mp 150 °C dec. Anal. Calcd for C$_{80}$H$_{50}$F$_{18}$N$_6$OP$_2$Ru$_2$: C, 55.95; H, 2.93; N, 4.89. Found: C, 56.78; H, 3.41; N, 4.74. FAB MS: 1720, M$^+$, 10; 1403, [M – CCPhC(CF$_3$)$_2$C(CN)$_2$]$^+$, 0.9; 744, [Ru[CCPhC(CF$_3$)$_2$C(CN)$_2$](PPh$_3$)(C$_5$H$_5$)]$^+$, 14; 429, [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$, 100. UV (CH$_2$Cl$_2$): 234 (ϵ 81 000), 274 (44 000), 350 (2000), 594 nm (5000). IR (Nujol mull): ν(CN) 2161 (m), 2008 (s, br) cm^{-1}; ν(CC) 1608 (m), 1588 (vw), 1570 (m), cm^{-1}; ν(CF) 1262 (s), 1250 (s), 1200

Table IV. Crystal and Refinement Data for Complexes 4 and 2a

	4	**2a**
formula	$C_{40}H_{32}Cl_2F_6N_3OPRu$	$C_{83}H_{53}F_{18}N_6P_2Ru_2$
M_r	887.6	1740.4
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (C_i^1, No. 2)	$P2_1/c$ (C_{2h}^5, No. 14)
a, Å	13.682 (2)	20.48 (1)
b, Å	15.616 (4)	19.378 (4)
c, Å	9.776 (4)	20.914 (3)
α, deg	97.97 (4)	90
β, deg	92.90 (3)	112.6 (3)
γ, deg	80.53 (2)	90
V, Å^3	2039.5	7662.6
D_{measd}, g cm^{-3}	1.48	1.48
Z	2	4
D_{calcd}, g cm^{-3}	1.445	1.509
$F(000)$	896	3492
cryst size, mm	0.10 × 0.20 × 0.50	0.08 × 0.10 × 0.20
μ, cm^{-1}	5.67	4.82
θ range, deg	1–22.5	1.5–20
no. of rflns measd	5135	5899
no. of unique rflns	5135	3644
criterion of observability	$2.5\sigma(I)$	$2.5\sigma(I)$
no. of obsd rflns	3883	1708
R	0.059	0.045
k	1.0	1.7
g	0.0050	0.0006
R_w	0.064	0.045
ρ_{max}, e Å^{-3}	0.72	0.31

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

atom	*x*	*y*	*z*
Ru	13415 (4)	33242 (3)	6186 (5)
P(1)	935 (1)	1939 (1)	327 (2)
F(1)	4323 (4)	1649 (3)	−2308 (5)
F(2)	5640 (4)	1772 (4)	−1104 (6)
F(3)	5204 (4)	2594 (4)	−2715 (6)
F(4)	4458 (5)	4107 (4)	1059 (6)
F(5)	5712 (5)	3102 (5)	745 (7)
F(6)	5289 (5)	3992 (4)	−759 (7)
N(1)	861 (4)	3423 (3)	−1364 (6)
N(2)	2714 (6)	2885 (6)	−3762 (8)
N(3)	2836 (8)	5084 (6)	−824 (10)
C(1)	1930 (7)	4290 (6)	2206 (8)
C(2)	1117 (7)	4741 (5)	1497 (8)
C(3)	245 (7)	4388 (6)	1728 (8)
C(4)	525 (7)	3722 (5)	2575 (7)
C(5)	1558 (7)	3653 (5)	2854 (8)
C(6)	544 (6)	3465 (5)	−2454 (8)
C(7)	154 (10)	3501 (8)	−3885 (9)
C(8)	2741 (5)	2954 (4)	−88 (6)
C(9)	3239 (6)	3379 (5)	−1195 (7)
C(10)	2970 (6)	3100 (6)	−2654 (9)
C(11)	3037 (7)	4356 (6)	−1002 (9)
C(12)	4270 (5)	2908 (5)	−648 (7)
C(13)	4852 (6)	2220 (6)	−1708 (9)
C(14)	4944 (8)	3543 (7)	110 (11)
C(15)	3642 (5)	2548 (5)	323 (7)
C(16)	3966 (4)	1963 (3)	1384 (5)
C(17)	4089 (4)	1056 (3)	1026 (5)
C(18)	4341 (4)	506 (3)	2042 (5)
C(19)	4470 (4)	864 (3)	3416 (5)
C(20)	4346 (4)	1770 (3)	3774 (5)
C(21)	4094 (4)	2320 (3)	2758 (5)
C(22)	742 (3)	1552 (4)	1963 (5)
C(23)	−168 (3)	1358 (4)	2302 (5)
C(24)	−283 (3)	1107 (4)	3593 (5)
C(25)	513 (3)	1051 (4)	4544 (5)
C(26)	1423 (3)	1246 (4)	4205 (5)
C(27)	1537 (3)	1496 (4)	2915 (5)
C(28)	1728 (4)	983 (3)	−584 (4)
C(29)	1894 (4)	171 (3)	−96 (4)
C(30)	2487 (4)	−539 (3)	−829 (4)
C(31)	2915 (4)	−439 (3)	−2050 (4)
C(32)	2750 (4)	373 (3)	−2538 (4)
C(33)	2156 (4)	1083 (3)	−1805 (4)
C(34)	−263 (3)	1900 (3)	−642 (5)
C(35)	−411 (3)	1208 (3)	−1656 (5)
C(36)	−1308 (3)	1235 (3)	−2406 (5)
C(37)	−2057 (3)	1954 (3)	−2142 (5)
C(38)	−1909 (3)	2646 (3)	−1128 (5)
C(39)	−1012 (3)	2619 (3)	−377 (5)
O(1)	5512 (29)	5546 (26)	4338 (38)
C(40)	6814 (26)	3977 (23)	3859 (71)
Cl(1)	7874 (10)	4475 (9)	4200 (14)
Cl(2)	7475 (13)	2910 (13)	3810 (17)

(s) cm^{-1}. Another minor green band (R_f 0.27) was collected (**15a**) and identified spectroscopically as an isomer of **15b**. IR (Nujol): ν(CN) 2165 s, 2047 vs cm^{-1}; ν(CC) 1613 w, 1577 m cm^{-1}; ν(CF) 1291 (sh), 1276 vs, 1237 (sh), 1216 (sh), 1198 s cm^{-1}; other peaks at 1482 w, 1437 m, 1358 m, 1320 m, 1158 w, 1128 w, 1113 m, 1097 m, 1072 w, 1054 w, 1037 w, 1000 w, 987 w, 946 m, 926 m, 878 w, 831 m, 818 w, 745 m, 719 m, 702 (sh), 693 m, 633 m cm^{-1}. ^{1}H NMR ($CDCl_3$): no signals detected. FAB MS (selected ions): 1720, $[M]^+$, 9; 1404*, $[M - C{=}CPhC(CF_3)_2C(CN)_2]^+$, 1; 812, $[1405 - PPh_3 - CF_3]^+$, 3; 744*, $[Ru[C{=}CPhC(CF_3)_2C(CN)_2](PPh_3)(C_5H_5)]^+$, 17; 429* $[Ru(PPh_3)(C_5H_5)]^+$, 100; 352*, $[Ru(PPh_2)(C_5H_5)]^+$, 16; 244*, $[RuPh(C_5H_5)]^+$, 13.

As noted below, complex **2a** converts into **15a**, and **2b** into **15b**, when placed in solution. Pure solutions **2a** or **2b**, when subjected to TLC, invariably show minor amounts of the corresponding isomers of **15**. The ESR spectra of all four complexes show a common broad absorption (g = 2.038, ΔH_{PP} = 31 G). None of the other seven bands present in the initial TLC separation were identified. A reaction carried out in CH_2Cl_2 gave none of the complexes **2** or **15**, and of the 16 products only PPh_3 was characterized (IR, ^{1}H NMR).

(b) Complexes **2a**, **2b**, and **15b** were isolated from the reaction of **4** (130 mg, 0.16 mmol) with dcfe (35 mg, 0.16 mmol) in benzene (20 mL). After 7 h the solvent was removed from the blue solution and the residue purified by prepreative TLC (petroleum ether/CH_2Cl_2 3/2). Three bands were collected and identified (IR, ^{1}H NMR, and FAB MS) as **2a** (R_f 0.8, purple), **2b** (R_f 0.7, blue), and **15b** (R_f 0.3, green).

Reaction of Complexes 2 with O$_2$. (a) A solution of **2a** (2 mg, 0.001 mmol) in benzene (5 mL) was saturated with O_2 and left under normal lighting conditions for 4 days. At this stage spot TLC indicated a significant proportion of **15a** present in solution. ESR spectroscopy confirmed the presence of a paramagnetic complex with a broad signal at g = 2.038.

(b) Similarly, a solution of **2b** (4 mg, 0.002 mmol) was left for 4 days under O_2. Spot TLC analysis of the solution indicated a significant amount of **15b** (an ESR signal was observed at g = 2.038) and a trace amount of **2a**.

(c) A solution of **2a** (1 mg, 0.0005 mmol) in CH_2Cl_2 was supported on silica (287 mg, 200 mesh) and left in the dark for 4 days. At this stage the silica had a green coloration and the adsorbed complex was removed (CH_2Cl_2/MeOH) and evaporated to dryness under reduced pressure. The residue was separated by TLC (petroleum ether/CH_2Cl_2/acetone 4/2/1) to give a green band (R_f 0.7) identified (spot TLC, FAB MS) as **15b** and a blue-green band (R_f 0.65) identified (spot TLC, FAB MS) as **15a**.

Crystallography. Intensity data were measured at room temperature on an Enraf-Nonius CAD4F diffractometer equipped with Mo Kα (graphite-monochromatized) radiation (λ = 0.71073 Å) with the use of the $\omega/2\theta$ scan technique for **4** and the ω/θ scan technique for **2a**. The intensities of three standard reflections were measured after every 3600 s of X-ray exposure time, and these indicated that no significant decomposition of either crystal occurred during their respective data collections. Routine corrections were made for Lorentz and polarization effects[18] (with the use of SUSCAD for **2a**) and for absorption by employing an

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[18] Programs used in the crystal structure determinations were as follows: SUSCAD, data reduction program for the CAD4 diffractometer, University of Sydney, 1976; PREABS and PROCES, data reduction programs for the CAD4 diffractometer, University of Melbourne, 1981; SHELX, program for crystal structure determination, University of Cambridge, 1976.

Table VI. Fractional Atomic Coordinates (×10^4) for $[Ru[\overline{C{=}CPhC(CF_3)_2C}(CN)_2](PPh_3)(\eta\text{-}C_5H_5)]_2[\mu\text{-}(CN)_2C{=}C(CF_3)_2]$ (2a)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Ru(1)	1435 (1)	3281 (1)	1291 (1)	C(26)	1454 (10)	3905 (9)	−606 (9)
Ru(2)	2258 (1)	6672 (1)	2513 (1)	C(27)	2080 (14)	3876 (14)	−861 (14)
P(1)	2096 (3)	2277 (3)	1517 (3)	C(28)	790 (13)	4171 (13)	−1145 (13)
P(2)	3286 (3)	7321 (3)	2934 (3)	C(29)	1686 (10)	4220 (9)	117 (8)
F(1)	1872 (7)	3505 (6)	−1451 (6)	C(30)	1231 (12)	4807 (11)	240 (10)
F(2)	2263 (7)	4506 (7)	−1001 (6)	C(31)	2404 (13)	4493 (11)	457 (11)
F(3)	2661 (7)	3576 (6)	−423 (6)	C(32)	1113 (7)	2556 (5)	−596 (6)
F(4)	887 (7)	4827 (7)	−1348 (6)	C(33)	1585 (7)	2112 (5)	−725 (6)
F(5)	276 (7)	4207 (6)	−930 (6)	C(34)	1347 (7)	1484 (5)	−1058 (6)
F(6)	570 (7)	3799 (7)	−1731 (6)	C(35)	637 (7)	1299 (5)	−1262 (6)
F(7)	734 (8)	6238 (7)	3627 (9)	C(36)	165 (7)	1743 (5)	−1133 (6)
F(8)	1032 (9)	5410 (8)	4368 (10)	C(37)	404 (7)	2371 (5)	−800 (6)
F(9)	1074 (9)	6456 (8)	4718 (10)	C(38)	3113 (8)	8249 (6)	2730 (8)
F(10)	2397 (9)	5336 (8)	5247 (8)	C(39)	3388 (8)	8606 (6)	2310 (8)
F(11)	2383 (10)	6396 (8)	5498 (8)	C(40)	3242 (8)	9306 (6)	2177 (8)
F(12)	3118 (8)	6034 (7)	5120 (7)	C(41)	2821 (8)	9651 (6)	2463 (8)
F(13)	4387 (13)	5622 (14)	3032 (16)	C(42)	2546 (8)	9294 (6)	2883 (8)
F(13′)	4372 (19)	5508 (20)	3410 (22)	C(43)	2692 (8)	8594 (6)	3016 (8)
F(14)	4908 (16)	4779 (14)	3809 (16)	C(44)	3909 (8)	7086 (8)	2547 (9)
F(14′)	5271 (32)	4774 (26)	3437 (32)	C(45)	3646 (8)	6827 (8)	1873 (9)
F(15)	5072 (17)	5011 (14)	2842 (17)	C(46)	4111 (8)	6647 (8)	1557 (9)
F(15′)	4572 (39)	5277 (34)	2386 (36)	C(47)	4838 (8)	6726 (8)	1915 (9)
F(16)	3904 (12)	3283 (13)	2716 (14)	C(48)	5101 (8)	6986 (8)	2589 (9)
F(16′)	4930 (20)	3808 (17)	2609 (19)	C(49)	4637 (8)	7166 (8)	2905 (9)
F(17)	4334 (12)	3810 (11)	2018 (13)	C(50)	3838 (7)	7313 (8)	3848 (5)
F(17′)	3804 (15)	3351 (17)	2265 (18)	C(51)	3980 (7)	6679 (8)	4191 (5)
F(18)	4937 (13)	3621 (10)	3135 (13)	C(52)	4431 (7)	6647 (8)	4888 (5)
F(18′)	4426 (35)	3563 (29)	3329 (33)	C(53)	4740 (7)	7248 (8)	5242 (5)
N(1)	889 (10)	5213 (10)	315 (9)	C(54)	4597 (7)	7882 (8)	4899 (5)
N(2)	2968 (11)	4678 (9)	745 (10)	C(55)	4146 (7)	7914 (8)	4202 (5)
N(3)	1068 (13)	5066 (12)	2794 (13)	C(56)	1625 (8)	6720 (9)	1375 (7)
N(4)	3203 (15)	4893 (13)	4133 (13)	C(57)	1220 (8)	6379 (9)	1670 (7)
N(5)	2290 (8)	3837 (8)	1791 (7)	C(58)	1089 (8)	6828 (9)	2117 (7)
N(6)	2782 (8)	5804 (8)	2561 (8)	C(59)	1413 (8)	7447 (9)	2099 (7)
C(1)	2714 (6)	2096 (8)	1090 (6)	C(60)	1744 (8)	7380 (9)	1640 (7)
C(2)	3087 (6)	2655 (8)	979 (6)	C(61)	2248 (11)	6457 (10)	3450 (11)
C(3)	3597 (6)	2547 (8)	699 (6)	C(62)	2118 (10)	6771 (11)	3984 (9)
C(4)	3733 (6)	1881 (8)	530 (6)	C(63)	1949 (15)	6119 (13)	4325 (14)
C(5)	3360 (6)	1322 (8)	641 (6)	C(64)	1165 (16)	6055 (17)	4243 (17)
C(6)	2851 (6)	1430 (8)	922 (6)	C(65)	2437 (17)	5972 (15)	4987 (16)
C(7)	1563 (7)	1498 (6)	1360 (8)	C(66)	2128 (15)	5678 (14)	3724 (13)
C(8)	1489 (7)	1162 (6)	1919 (8)	C(67)	1525 (16)	5311 (14)	3198 (15)
C(9)	1059 (7)	579 (6)	1805 (8)	C(68)	2716 (18)	5241 (16)	3951 (14)
C(10)	702 (7)	333 (6)	1133 (8)	C(69)	2054 (9)	7491 (6)	4168 (8)
C(11)	776 (7)	670 (6)	575 (8)	C(70)	1428 (9)	7854 (6)	3827 (8)
C(12)	1206 (7)	1252 (6)	688 (8)	C(71)	1382 (9)	8549 (6)	3979 (8)
C(13)	2676 (7)	2186 (7)	2441 (5)	C(72)	1962 (9)	8881 (6)	4472 (8)
C(14)	3137 (7)	1625 (7)	2653 (5)	C(73)	2588 (9)	8518 (6)	4813 (8)
C(15)	3573 (7)	1546 (7)	3350 (5)	C(74)	2635 (9)	7823 (6)	4661 (8)
C(16)	3548 (7)	2027 (7)	3836 (5)	C(75)	2770 (12)	4189 (10)	2102 (10)
C(17)	3087 (7)	2588 (7)	3625 (5)	C(76)	3064 (10)	5305 (11)	2510 (10)
C(18)	2651 (7)	2667 (7)	2927 (5)	C(77)	3330 (13)	4643 (11)	2473 (11)
C(19)	772 (7)	3516 (7)	1917 (6)	C(78)	4037 (13)	4493 (11)	2743 (11)
C(20)	544 (7)	3939 (7)	1343 (6)	C(79)	4653 (21)	5017 (19)	3192 (21)
C(21)	292 (7)	3526 (7)	763 (6)	C(80)	4297 (18)	3760 (15)	2628 (17)
C(22)	364 (7)	2848 (7)	978 (6)	C(81)	4833 (27)	9824 (17)	4320 (18)
C(23)	661 (7)	2842 (7)	1691 (6)	C(82)	4295 (17)	9987 (16)	4808 (24)
C(24)	1505 (9)	3483 (8)	349 (9)	C(83)	4261 (31)	9870 (24)	4236 (27)
C(25)	1351 (9)	3237 (10)	−268 (9)	C(83′)	5459 (24)	9895 (18)	4573 (23)

analytical procedure for **4**;[18] an absorption correction was not applied for **2a** owing to the small size of the crystal. Relevant crystal data are summarized in Table IV.

The structure of **4** was solved by normal heavy-atom methods, and the positions of the Ru atoms in **2a** were obtained from the EEES direct-methods routine of SHELX.[18] The structure of **4** was refined by a full-matrix least-squares procedure based on F,[18] and for **2a**, a blocked-matrix procedure was employed. In **4**, the phenyl groups were refined as hexagonal rigid groups, and in **2a**, the phenyl groups and the Cp groups were refined as hexagonal and pentagonal rigid groups, respectively. Anisotropic thermal parameters were introduced for non-hydrogen (and non-phenyl) atoms in **4** and for the Ru, P, and most of the F atoms in **2a**; all other atoms were refined with isotropic thermal parameters. The fluorine atoms F(13)–F(18) in **2a** were found to be disordered over two sites, and thus the occupancy factors of these F atoms were refined. At convergence, the disordered F atoms had occupancies 0.62 (2) (F) and 0.38 (2) (F′); as a consequence of the disorder, the F(13)–F(18) atoms were refined with isotropic thermal parameters only. In the crystal lattice of **4**, there are H_2O and CH_2Cl_2 solvent molecules so that the ratio complex/H_2O/CH_2Cl_2 is 1/1/1. In **2a**, a number of peaks were located about a center of inversion at $^1/_2$, 0, $^1/_2$), and these were included and refined as a benzene molecule disordered over two sites with a multiplicity parameter of 0.55. Hydrogen atoms were included in the model of **4** at their calculated positions but were not included in the refinement of **2a**. A weighting scheme of the form $w = k/[\sigma^2(F) + gF^2]$ was included, and the refinement continued until convergence (maximum shift/esd <0.001) for both **4** and **2a**; refinement details are listed in Table IV.

Scattering factors for neutral Ru (corrected for f' and f'') were from ref 19, and values for the remaining atoms were those in-

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corporated in SHELX.[18] Data solution and refinements were performed with the SHELX program system on the University of Adelaide's Cyber (**2a**) and VAX11/780 (**4**) computer systems.

Fractional atomic coordinates are listed in Tables V and VI; the numbering schemes used are shown in Figures 1 and 2. Selected interatomic bond distances and angles are given in Table I.

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Registry No. **2a**, 129571-03-5; **2b**, 129646-59-9; **3**, 124225-89-4; **4**, 129571-05-7; **5**, 129571-06-8; **6**, 129571-07-9; **7**, 129571-08-0; **8**, 129571-09-1; **9**, 129571-10-4; **10a**, 129571-11-5; **10b**, 129646-60-2; **11**, 129571-12-6; **12**, 129571-13-7; **13a**, 129571-14-8; **13b**, 129646-61-3; **13c**, 129571-15-9; **15a**, 129571-16-0; **15b**, 129646-62-4; dcfe, 1113-69-5; TCNE, 670-54-2; $Ru(C_2Ph)(PPh_3)_2(\eta^5\text{-}C_5H_5)$, 58355-23-0; $[Ru[C{\equiv}CPhC(CF_3)_2C(CN)_2](PPh_3)(\eta^5\text{-}C_5H_5)]_2[\mu\text{-}(NC)_2C_6F_4\text{-}p]$, 129571-17-1; MeCN, 75-05-8; acrylonitrile, 107-13-1; 1,2,4,5-tetracyanobenzene, 712-74-3; phthalodinitrile, 91-15-6; tetrafluorophthalodinitrile, 1835-65-0; tetrafluoroterephthalonitrile, 1835-49-0; fumaronitrile, 764-42-1.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom parameters, and bond distances and angles for **2a** and **4** and listings of spectroscopic (UV/visible, FAB MS, and IR) data for organonitrile complexes and electrochemical and UV/visible data for nitrile ligands (19 pages); listings of observed and calculated structure factors for **2a** and **4** (32 pages). Ordering information is given on any current masthead page.

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Selective Lithiation of 1-Bromo-2-((trimethylstannyl)methyl)benzene: Synthesis of 1-Bromo-2-(lithiomethyl)benzene, 1-Lithio-2-((trimethylstannyl)methyl)benzene, and α,2-Dilithiotoluene

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Reactions of 1-bromo-2-((trimethylstannyl)methyl)benzene (1) with *n*-butyllithium and *tert*-butyllithium have been investigated. With *n*-butyllithium in tetrahydrofuran (THF) at −70 °C, the only observed process was lithium–tin exchange, yielding 1-bromo-2-(lithiomethyl)benzene (2). In contrast, lithium–halogen exchange occurred when 1 was treated with *tert*-butyllithium in diethyl ether at −80 °C to give 1-lithio-2-((trimethylstannyl)methyl)benzene (3). α,2-Dilithiotoluene could be prepared in high yield from 3 and *tert*-butyllithium in either diethyl ether (room temperature) or THF (−80 °C).

Introduction

Organolithium compounds are generally prepared by traditional methods such as lithium–halogen exchange and metalation.[1] However, when these methods are not selective or mild enough, the lithium–tin exchange reaction often provides a good alternative for the synthesis of the required compound.[2] The mechanism suggested for this transmetalation involves stannate complexes, for which direct evidence was recently provided by ^{119}Sn NMR studies on mixtures of tetramethylstannane and methyllithium or phenyllithium in THF/hexamethylphosphoric triamide (HMPT).[3] When the starting material has both a halogen and a trimethylstannyl group as substituents, lithium–tin exchange can compete effectively with lithium–halogen exchange. This has been demonstrated by the reaction between 1,3-dibromo-5-(trimethylstannyl)benzene and *n*-butyllithium in diethyl ether at −78 °C, which predominantly yielded 1,3-dibromo-5-lithiobenzene.[4] We now report selective lithiation of 1-bromo-2-((trimethylstannyl)methyl)benzene (**1**) to 1-bromo-2-(lithiomethyl)benzene (**2**), 1-lithio-2-((trimethylstannyl)methyl)benzene (**3**), or α,2-dilithiotoluene (**4**). The last compound had previously been detected in small amounts in metalations of toluene or benzyllithium by *n*-butyllithium/tetramethylethylenediamine (TMEDA).[5]

Results

Reactions of 1 with *n*-BuLi. A series of reactions between **1** and *n*-BuLi was conducted under various conditions (Table I and Scheme I). In a typical experiment, **1** was added to *n*-BuLi in diethyl ether (with some *n*-hexane, see Experimental Section) at the indicated tem-

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