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Reactions of Transition-Metal σ-Acetylide Complexes. 2. Cycloaddition and Subsequent Reactions of Tetracyanoethylene with Some (η-Cyclopentadienyl)ruthenium–Tertiary Phosphine Complexes: X-ray Structure of $\mathrm{Ru\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}(dppe)(\eta\text{-}C_5H_5){\cdot}0.5CHCl_3}$

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Reactions between $\mathrm{Ru(C_2R)(L)(L')(\eta\text{-}C_5H_5)}$ [R = Me, Ph; L = $\mathrm{PPh_3}$; L′ = CO, $\mathrm{PPh_3}$, $\mathrm{P(OPh)_3}$; LL′ = dppe; not all combinations] and tetracyanoethylene give deep green paramagnetic compounds and cyclobutenyl $\mathrm{Ru[\overline{C{=}CRC(CN)_2C}(CN)_2](L)(L')(\eta\text{-}C_5H_5)}$, butadienyl $\mathrm{Ru\{C[{=}C(CN)_2]CRC{=}C(CN)_2\}(L)(L')(\eta\text{-}C_5H_5)}$, or "allylic" $\mathrm{Ru[\eta^3\text{-}C(CN)_2CRC{=}C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)}$ complexes; for L′ = $\mathrm{PPh_3}$, the latter is the only product isolated. The cyclobutenyl complexes transform rather readily into the butadienyl complexes, which are also formed by reaction of the "allyl" complexes with two-electron-donor ligands (CO, CN-*t*-Bu). In solution, NMR studies indicate the presence of rotational isomers in a solvent-dependent equilibrium. The X-ray structure of $\mathrm{Ru\{C[{=}C(CN)_2]CPhC{=}C(CN)_2\}(dppe)(\eta\text{-}C_5H_5)}$ is reported: crystals are triclinic of space group $P\bar{1}$ with $a = 10.323$ (5) Å, $b = 12.157$ (8) Å, $c = 16.64$ (1) Å, $\alpha = 91.12$ (6)°, $\beta = 105.55$ (4)°, $\gamma = 95.93$ (5)°; $Z = 2$. The structure was refined by using 4290 data with $I > 2.5\sigma(I)$ to $R = 0.036$ and $R_w = 0.039$. Important bond lengths (Å) are as follows: Ru–C = 2.068 (4), butadienyl C=C = 1.346, 1.370 (6); C–C = 1.484 (6), showing localization of the 1,3-diene system; the $\mathrm{C_4}$ skeleton is significantly bent (torsion angle between C=C planes = 80.6°).

Introduction

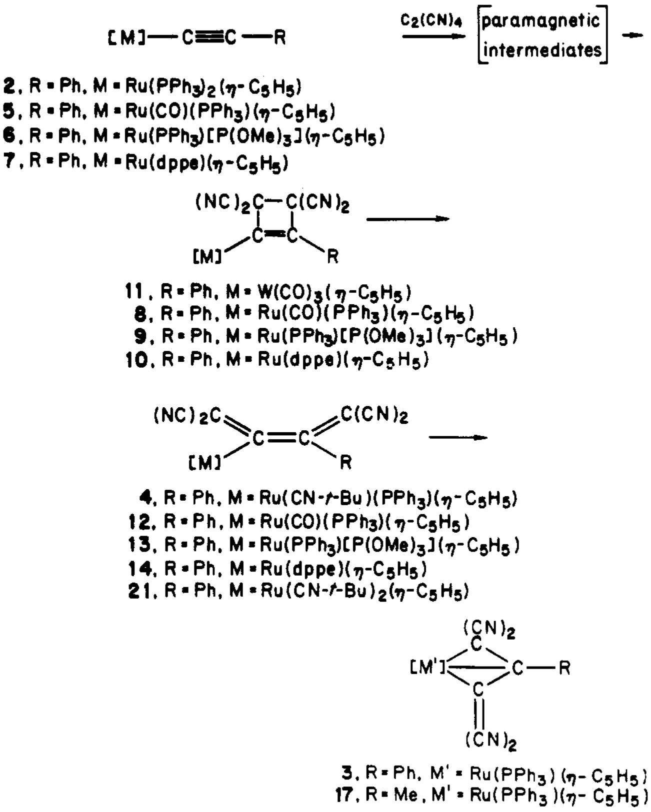
The previous paper described the reaction between tetracyanoethylene and $\mathrm{W(C_2Ph)(CO)_3(\eta\text{-}C_5H_5)}$ (**1**, Scheme I). We have also reported briefly that the reaction between the cyanoolefin and $\mathrm{Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)}$ (**2**) affords directly $\mathrm{Ru(PPh_3)[\eta^3\text{-}C(CN)_2CPhC{=}C(CN)_2](\eta\text{-}C_5H_5)}$ (**3**), which with two-electron-donor ligands, L, gives the butadienyl complexes $\mathrm{Ru\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}(L)(PPh_3)(\eta\text{-}C_5H_5)}$. In this paper we describe these reactions in detail, together with the X-ray structure of the butadienyl complex $\mathrm{Ru\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}(dppe)(\eta\text{-}C_5H_5)}$.

Results and Discussion

Addition of tetracyanoethylene to $\mathrm{Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)}$ (**2**) in benzene gives a deep green solution which slowly lightens in color, with the deposition of orange crystals of $\mathrm{Ru[\eta^3\text{-}C(CN)_2CPhC{=}C(CN)_2](PPh_3)(\eta\text{-}C_5H_5)}$ (**3**).[2] Addition of CN-*t*-Bu to **3** afforded the butadienyl complex $\mathrm{Ru\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}(CN\text{-}\mathit{t}\text{-}Bu)(PPh_3)(\eta\text{-}C_5H_5)}$ (**4**). In contrast, similar reactions of acetylide complexes containing only one $\mathrm{PPh_3}$ ligand, $\mathrm{Ru(C_2Ph)(L)(PPh_3)(\eta\text{-}C_5H_5)}$ [L = CO (**5**) or $\mathrm{P(OMe)_3}$ (**6**)], or $\mathrm{Ru(C_2Ph)(dppe)(\eta\text{-}C_5H_5)}$ (**7**) give cyclobutenyl complexes, which more or less quickly isomerize to the corresponding butadienyl complexes.

The first-formed, intensely colored solutions contain a paramagnetic compound, for several examples of which we obtained ESR spectra: that obtained from the reaction of $\mathrm{Ru(C_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)}$ and tetracyanoethylene is shown in Figure 1. As with the tungsten complex, these spectra do not resemble that of $[\mathrm{C_2(CN)_4}]^{-\cdot}$[3] nor those of the radical intermediates found in some other reactions between the cyanoolefin and metal complexes.[4] Since the latter involves products formed by M–M or M–C bond

Scheme I. Reactions of Tetracyanoethylene with Some Transition-Metal σ-Acetylide Complexes



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(1) Part 1: M. I. Bruce, T. W. Hambley, M. R. Snow, and A. G. Swincer, preceding paper in this issue.

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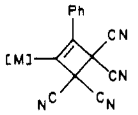
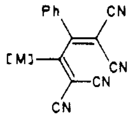
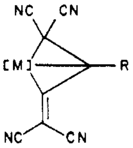
Table I. ν(CN) and ν(C=C) Absorptions of Some Cyclobutenyl, Butadienyl, and η^3-Cyanocarbon Complexes

[M]	R	no.	ν(CN)	ν(C=C)
				
$W(CO)_3(\eta\text{-}C_5H_5)$		11	2244 (vw)	1489 (w)
$Ru(CO)(PPh_3)(\eta\text{-}C_5H_5)$		8	2218 (w)	1611 (vw), 1572 (vw), 1525 (w)
$Ru[P(OMe)_3](PPh_3)(\eta\text{-}C_5H_5)$		9	2239 (vw)	1609 (vw), 1587 (vw), 1568 (w)
$Ru(dppe)(\eta\text{-}C_5H_5)$		10	2235 (vw), 2210 (vw, br)	1545 (w)
$Fe(CO)_2(\eta\text{-}C_5H_5)$			2243 (vw)	1601 (vw), 1583 (w), 1557 (w)
				
$W(CO)_3(\eta\text{-}C_5H_5)$			2222 (m), 2210 (m)	1522 (s)
$Ru(CN\text{-}t\text{-}Bu)(PPh_3)(\eta\text{-}C_5H_5)$		4	2224 (m), 2216 (m), 2209 (m)	1510 (m), 1503 (sh)
$Ru(CO)(PPh_3)(\eta\text{-}C_5H_5)$		12	2226 (m), 2219 (m), 2212 (m)	1516 (m)
$Ru[P(OMe)_3](PPh_3)(\eta\text{-}C_5H_5)$		13	2248 (vw), 2225 (w), 2212 (m), 2202 (w)	1525 (m)
$Fe(CO)_2(\eta\text{-}C_5H_5)$			2220 (m), 2207 (m), 2201 (m)	1533 (m), 1528 (sh)
$Ru(dppe)(\eta\text{-}C_5H_5)$		14	2219 (w), 2208 (w), 2199 (w)	1520 (m)
$Ru(CN\text{-}t\text{-}Bu)_2(\eta\text{-}C_5H_5)$		21	2223 (m), 2216 (sh)	1530 (m)
				
$W(CO)_2(\eta\text{-}C_5H_5)$	Ph		2232 (s), 2222 (m)	1586 (s)
$Ru(PPh_3)(\eta\text{-}C_5H_5)$	Ph	3	2215 (s)	1590 (s)
$Ru(PPh_3)(\eta\text{-}C_5H_5)$	Me	17	2225 (s), 2219 (sh)	1615 (s), 1587 (m)
$Ru(PPh_3)(\eta\text{-}C_5H_5)$	{Ru}[a]	18	2210 (s)	1620 (s), 1587 (m)
$Ru(PPh_3)(\eta\text{-}C_5H_5)$	CH_2[b]	19	2220 (s)	1613 (s)

[a] {Ru} = $CH_2CH_2C_2Ru(PPh_3)_2(\eta\text{-}C_5H_5)$. [b] Binuclear allylic complex.

cleavage, this is not surprising. Figure 1 also shows a simulated spectrum that correlates well with the observed spectrum; this was obtained by assuming coupling of the unpaired electron to four nitrogens equally (a_N = 1.57 G) and to one phosphorus nucleus (a_P = 4.48 G). Compared with that of the phenylacetylide derivative, the line width of the methylacetylide derivative is somewhat greater, presumably as a result of an unresolved coupling of the CH_3 protons. We have been unable to characterize this species further, but the coupling to only one ^{31}P nucleus suggests that the ready loss of a PPh_3 ligand, which is such a feature of $RuX(PPh_3)_2(\eta\text{-}C_5H_5)$ chemistry, is also occurring in this reaction. This observation also explains why the allylic complexes are observed as major products in the reactions of $Ru(C_2R)(PPh_3)_2(\eta\text{-}C_5H_5)$, whereas the cyclobutenyl/butadienyl pairs are obtained from 5–7. The ESR spectrum of the initial product from the reaction of 7 differs from that shown in Figure 1, and we have been unable to find a satisfactory interpretation of it.

As found with $W(C_2Ph)(CO)_3(\eta\text{-}C_5H_5)$, but in contrast with the reaction of 2, σ-cyclobutenyl complexes 8–10 are the first-formed isolable complexes from the reactions of alkynylruthenium complexes containing other than two PPh_3 ligands. These compounds were identified by comparing their IR spectra (Table I) with that of the crystallographically characterized $W[\overline{C{=}CPhC(CN)_2C(CN)_2}](CO)_3(\eta\text{-}C_5H_5)$ (11). In all of the complexes studied, the ν(CN) absorption is weak or very weak, while in the olefinic region, weak to medium intensity bands between 1490 and 1610 cm^{-1} are assigned to ν(C=C). The 1:1 adduct formulation was confirmed by microanalytical results and the mass spectra, which all contained molecular ions. In solution, these compounds underwent the ring-opening reactions observed with the tungsten derivative, to give the corresponding butadienyl complexes 12–14; these reactions could be followed by ^1H NMR and also occurred in the solid state at room temperature in the case

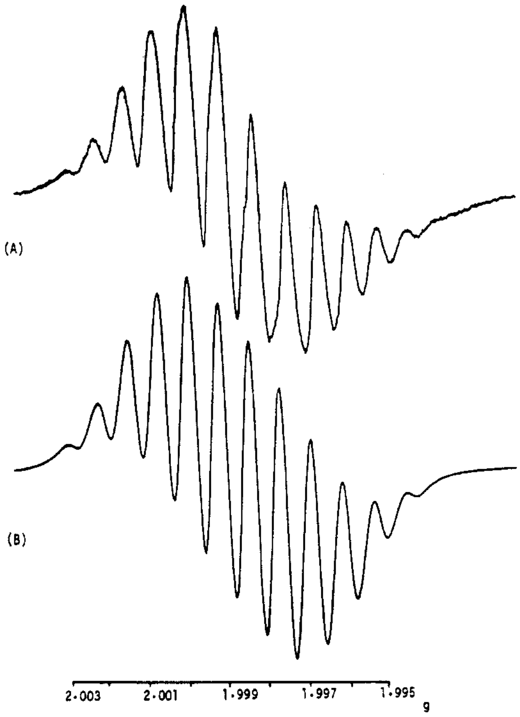
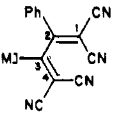
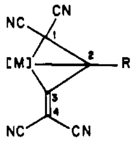


Figure 1. (A) ESR spectrum of deep green solution obtained immediately after mixing equimolar proportions of $C_2(CN)_4$ and $Ru(C_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$ in benzene. (B) Simulated spectrum of one electron coupled to four nitrogen nuclei (a_N = 1.57 G) and one phosphorus nucleus (a_P = 4.48 G).

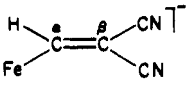
Table II. ^{13}C NMR Spectra of Some Cyanocarbon Complexes[a]

[M]	R	no.	C(1)	C(2)	C(3)	C(4)
						
$W(CO)_3(\eta\text{-}C_5H_5)$			77.4 (s)	182.8 (s)	221.7 (s)	99.8 (s)
$Ru(CN\text{-}t\text{-}Bu)(PPh_3)(\eta\text{-}C_5H_5)$		4	73.8 (s)	178.1 (s)	224.3 (d (9))	95.2 (s)
$Ru(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (A)		12	75.7 (s)	181.2 (s)	215.6 (d (12))	94.0 (d (3))
(B)			76.2 (s)	184.7 (s)	213.4 (d (10))	95.0 (d (3))
$Ru[P(OMe)_3](PPh_3)(\eta\text{-}C_5H_5)$		13	*b*	177.2 (m)	223.6 (d (15))	97.4 (m)
$Fe(CO)_2(\eta\text{-}C_5H_5)$			74.9 (s)	181.2 (s)	215.1 (s)	98.0 (s)
$Ru(dppe)(\eta\text{-}C_5H_5)$		14	73.9 (m)	181.9 (m)	225.7 (m)	95.1 (m)
$Ru(CN\text{-}t\text{-}Bu)_2(\eta\text{-}C_5H_5)$		15	69.3 (s)	179.7 (s)	226.2 (s)	90.8 (s)
						
$W(CO)_2(\eta\text{-}C_5H_5)$	Ph		79.4 (s)	4.7 (s)	206.6 (s)	*c*
$Ru(PPh_3)(\eta\text{-}C_5H_5)$	Ph	3	85.1 (d (7))	7.3 (d (6))	218.8 (d (15))	66.7 (d (3))
$Ru(PPh_3)(\eta\text{-}C_5H_5)$	Me	17	82.9 (m)	11.0 (d (6))	218.3 (d (15))	63.1 (d (3))
$Ru(PPh_3)(\eta\text{-}C_5H_5)$	{Ru}[d]	18	82.0 (d (7))	10.6 (d (5))	219.0 (d (15))	66.7 (d (3))

[a] Chemical shifts (δ); coupling constants (Hz) in parentheses. [b] Under $CDCl_3$ resonance. [c] Not detected. [d] {Ru} = $CH_2CH_2C_2Ru(PPh_3)_2(\eta\text{-}C_5H_5)$.

of **10**. Unfortunately, these reactions all proceeded before full ^{13}C NMR spectra could be accumulated, so that the chemical shifts of the cyclobutenyl ring carbons could not be determined.

The butadienyl complexes **12**–**14** have been fully characterized by analysis and from a comparison of their spectroscopic properties with those of the tungsten analogue and of $Ru\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}(CN\text{-}t\text{-}Bu)(PPh_3)(\eta\text{-}C_5H_5)$ (**4**) which has been the subject of an X-ray study.[2] The IR spectra (Table I) are characterized by stronger ν(CN) bands than found for the cyclobutenyl complexes, with two or three medium intensity absorptions generally being found between 2200 and 2225 cm^{-1}. The ν(C=C) absorptions are also stronger than those of **8**–**10**, generally occurring between 1510 and 1530 cm^{-1}. In their ^{13}C NMR spectra (Table II), the butadienyl complexes contain resonances in the regions δ 69.3–77.4, 94.0–99.8, 177.2–184.7, and 213.4–226.2, which are assigned to the four carbons of the C_4 backbone. The resonances with highest chemical shift are coupled to ^{31}P, if present, and are therefore assigned to the metal-bonded carbon C(3). Two complexes having some features in common with the butadienyl derivatives are $[Fe\{C^{\alpha}H{=}C^{\beta}(CN)_2\}(CO)_4]^-$ (**15**)[5] and $Mo[C^{\alpha}H{=}CH(CN)][C(CF_3){=}CH_2](\eta\text{-}C_5H_5)_2$ (**16**):[6] in these, C^{α} resonates at δ 228.2 and 200.1, respectively. The chemical shifts of these carbons lie between those of α-carbons in metal σ-acetylide complexes (δ 90–116) and metal carbene complexes (δ 300–360) and indicate that these nuclei are considerably electron deficient.



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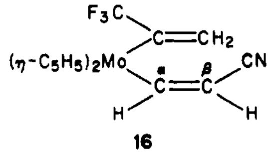

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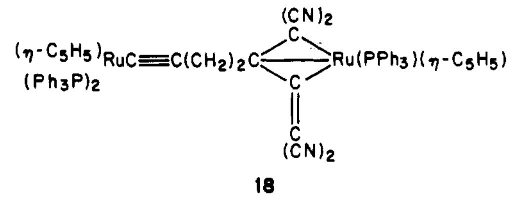
In the iron complex cited above, C^{β} resonates at δ 93.9; the similarity to C(4) in our complexes is obvious, and we therefore assign the resonances between δ 94.0 and 99.8 to this carbon. In **8**, this is further supported by the observation of a 3-Hz coupling to ^{31}P through the C=C double bond. The resonances at δ ca. 75 are assigned to C(1) by comparison with other dicyanomethylene derivatives.[7] By elimination, resonances at δ ca. 180 have to be assigned to C(2), although the unusually high chemical shift of these carbons is not understood at present.

As mentioned above, an "allylic" complex (**3**) was isolated from the reaction between **2** and $C_2(CN)_4$. A similar reaction of tetracyanoethylene with $Ru(C_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)$ gave **17**, while with $[CH_2C_2Ru(PPh_3)_2(\eta\text{-}C_5H_5)]_2$ complexes **18** and **19** were obtained from reactions in which



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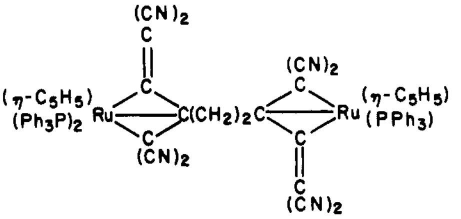

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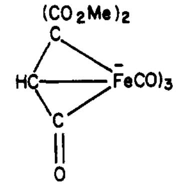

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equimolar or excess $C_2(CN)_4$, respectively, was employed. Apart from microanalytical results, these compounds could be identified by their spectroscopic properties. One or two strong ν(CN) bands (between 2210 and 2232 cm^{-1}) and strong ν(C=C) absorptions (1585–1620 cm^{-1}) were present in their IR spectra. In addition to resonances associated with the C_5H_5 and PPh_3 ligands, the ^{13}C NMR spectra contain characteristic resonances at δ 4.7–11.0, 63.1–66.7, 79.4–85.1, and 206.6–219.0 which are assigned to C(2), C(4),

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(5) T. H. Mitsudo, H. Watanabe, Y. Watanabe, N. Nitani, and Y. Takegami, *J. Chem. Soc., Dalton Trans.*, 395 (1979).

(6) H. Scordia, R. Kergoat, M. M. Kubicki, and J. E. Guerchais, *J. Organomet. Chem.*, **249**, 371 (1983).

(7) R. B. King and S. P. Diefenbach, *Inorg. Chem.*, 18, 63 (1979).

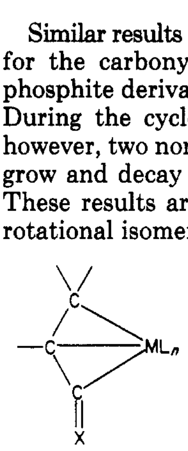
C(1) and C(3), respectively (Table II). All show coupling to ^{31}P, the largest being to the lowest field resonance; assuming that the strongest coupling will be to the carbon with the shortest M–C distance, we therefore assign these resonances to C(3) in accord with the structural determination of **3**. Although the "inner" carbons of η^3-allyl complexes normally resonate at lower field than do the "outer" carbons,[8] we note that in $[Fe(CO)_3\{\eta^3\text{-}C(CO_2Me)_2CHC{=}O\}]^-$ (**20**), which is structurally related to the present complexes, the central carbon resonates at δ 24.4, whereas the $C(CO_2Me)_2$ and C=O carbons are found at δ 49.7 and 246.0, respectively.[9] Consequently we are inclined to assign the highest field signals between δ 4.7 and 11.0 to C(2) and those between δ 79.4 and 85.1 to C(1), leaving the resonances at δ ca. 65 to be assigned to the central carbon [C(4)] of the dicyanomethylene substituent. Couplings to ^{31}P are 5–7 Hz for C(1) and C(2) and 3 Hz for C(4). To a certain extent these assignments are unsatisfactory, in that the central carbons of the allylic systems have unusually high chemical shifts; reversal of the C(1) and C(2) assignments is not unlikely when further data are obtained.

As discussed in the previous paper, the structural and ^{13}C NMR parameters for these complexes are best interpreted in terms of methylenemetallabicyclobutane, allenylmethyl, or allylic formulations. Lewis base ligands displace two of the three metal-bonded carbons, leaving the cyanocarbon ligand (now a butadienyl group) attached by the carbon which is nearest the metal atom in the allylic precursor. To some extent, the metal-bonded carbon remains electron deficient, as indicated by its large ^{13}C chemical shift; on the other hand, the Ru–C separation in **4** [2.074 (3) Å] is considerably longer than the corresponding distance in the "allylic" complex [1.919 (5) Å].

The reaction between **3** and CN-*t*-Bu, carried out at 70 °C, affords red $Ru\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}(CN\text{-}t\text{-}Bu)(PPh_3)(\eta\text{-}C_5H_5)$ (**4**), which was fully characterized by the X-ray study mentioned above.[2] Under more vigorous conditions (150 °C), the PPh_3 ligand in **4** is replaced by a second molecule of CN-*t*-Bu to give **21**. Carbonylation of **3** (53 atm, 120 °C, 17 h) afforded **12** in a reaction which is reversed by UV irradiation.

The resulting complexes were readily characterized by the usual methods, and by comparison with the same products obtained from $C_2(CN)_4$ and the acetylide complex, where appropriate. The NMR spectra of several of these complexes reveal the presence of isomers in solution. A study of models suggests that the butadienyl ligand does not rotate freely in most instances and we propose that the isomerism arises from the asymmetric ligand being locked in particular rotational conformations. Thus, the ^1H NMR spectrum of a freshly prepared solution of **4** contains singlet resonances for the Me and C_5H_5 protons at δ 1.33 and 4.62, respectively, which on standing (hours) or warming lose intensity as two new signals, at δ 1.26 and 4.54, grow. The two components are in equilibrium, although the final ratio is solvent dependent. For example, in $CDCl_3$, $(CD_3)_2CO$, and CD_3CN, the final ratios correspond to 1:2.3, 1:2.0 and 1:1.4, respectively, which ratios correlate with changes in solvent polarity. In $CDCl_3$ the ratio does not vary when the temperature is increased from 27 to 62 °C. In the ^{13}C NMR spectra only the C_5H_5 resonances are doubled. Only one isomer is recoverable in crystalline form.

Similar results are described in the Experimental Section for the carbonyl complex **12**, although the trimethyl phosphite derivative **13** exists in only one isomeric form. During the cyclobutene/butadiene isomerization of **9**, however, two nonisolable intermediates were observed to grow and decay before formation of **13** was completed. These results are best interpreted by the formation of rotational isomers, such as C and D. In solution, interconversion of these isomers is slow on the NMR time scale but fast enough to ensure that the sterically preferred isomer crystallizes from solution. Interaction of the polar cyanocarbon ligand with solvent molecules is a possible explanation of the solvent-dependent equilibrium ratios. In **21** the ^1H and ^{13}C resonances of the CN-*t*-Bu ligands are doubled, confirming the nonequivalence of the CN-*t*-Bu ligands resulting from the asymmetry of the butadienyl group. The ^1H and ^{13}C nuclei of the C_5H_5 group each resonate as singlets. The spectra of **14**, on the other hand, contain two equally intense C_5H_5 resonances, the relative intensities of which are not solvent dependent. In the solid state (see below), only one crystal form is found, and we suggest that in this instance the isomerism results from different conformations of the Ru(dppe) chelate ring. A similar situation exists for the cyclobutenyl complex **10**.



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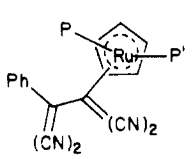

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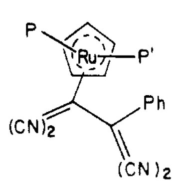

C

Structures of Complexes 4 and 14. The X-ray structure of **4** was reported earlier[2] and will only be discussed in detail here for the purposes of comparison with that of **14**. The unit cell of the latter contains **14** and chloroform of crystallization. There are no significant close contacts between any of the molecules. The solvent molecule is disordered over two sites related by a center of symmetry and thus has been included at half occupancy.

An ORTEP plot of the molecule is shown in Figure 2. The ruthenium is coordinated by the cyclopentadienyl [Ru–C(av) = 2.235 Å] and dppe ligands [Ru–P = 2.280 (1), 2.340 (1) Å], and the 1,1,4,4-tetracyano-2-phenylbuta-1,3-dien-3-yl ligand. The coordination geometry is distorted octahedral and is similar to those of many other similar complexes that have been studied.[10] This includes a slight asymmetry in the bonding of the C_5H_5 ligand, which while approaching the limits of significance in the present structure, is nevertheless characteristic of these complexes. The origins of this phenomenon probably lie in the differing trans effects of the various ligands or in the interruption of conjugation in the C_5 ring shown by recent

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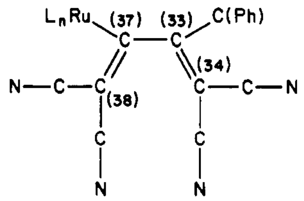
Table III. Structural Parameters of Butadienyl Groups in 4 and 14



	4 [L_nRu = Ru(CN-*t*-Bu)(PPh$_3$)(η-C$_5$H$_5$)]	14 [L_nRu = Ru(dppe)(η-C$_5$H$_5$)]
	Bond Distances (Å)	
Ru-C(37)	2.074 (3)	2.068 (4)
C(34)-C(33)	1.362 (4)	1.346 (6)
C(33)-C(37)	1.478 (4)	1.484 (6)
C(37)-C(38)	1.382 (5)	1.370 (6)
C(Ph)-C(33)	1.479 (5)	1.497 (6)
C-CN(av)	1.439	1.433
C-N(av)	1.142	1.134
	Bond Angles (deg)	
C(33)-C(34)-CN	121.4 (3), 126.3 (4)	122.7 (4), 124.3 (4)
NC-C(34)-CN	112.1 (3)	112.7 (4)
C(34)-C(33)-C(37)	117.9 (3)	124.3 (4)
C(34)-C(33)-C(Ph)	123.2 (3)	119.9 (4)
C(37)-C(33)-C(Ph)	118.9 (3)	115.6 (3)
C(33)-C(37)-C(38)	112.8 (3)	114.4 (4)
C(33)-C(37)-Ru	124.7 (2)	119.5 (3)
C(38)-C(37)-Ru	122.5 (3)	124.4 (3)
C(37)-C(38)-CN	123.7 (4), 124.2 (4)	122.3 (4), 122.7 (4)
NC-C(38)-CN	112.0 (4)	114.8 (4)
C(34)-C-N	174.9 (4), 177.2 (4)	177.1 (5), 177.5 (6)
C(38)-C-N	174.5 (5)	175.0 (4), 178.5 (5)
	Torsion Angles (deg)	
Ru-C(37)-C(33)-C(Ph)	70.0	70.2
Ru-C(37)-C(33)-C(34)	111.7	112.9
Ru-C(37)-C(38)-CN	10.3, 169.0	3.2, 170.4
C(34)-C(33)-C(37)-C(38)	81.5	80.6
C(Ph)-C(33)-C(37)-C(38)	106.4	95.4

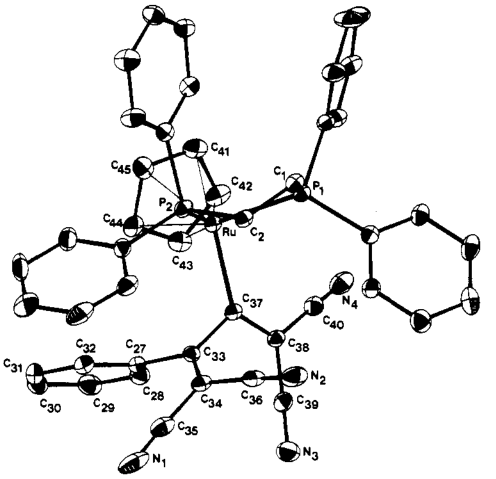


Figure 2. ORTEP plot of Ru{C[=C(CN)$_2$]CPh=C(CN)$_2$}(dppe)(η-C$_5$H$_5$) (16), showing atom numbering system.

accurate structural determinations[11] and theoretical calculations.[12]

In the present context, interest centers on the butadienyl ligands in 4 and 14, which are chemically the same and structurally similar. Table III summarizes the structural parameters in the two complexes. The Ru–C distances [2.068 (4) Å for 4 and 2.074 (3) Å for 14] are in accord with those found for other Ru–C(sp^2) bonds, for example, in Ru[C(R)=C(R)C(CF$_3$)=CH(CF$_3$)](PPh$_3$)(η-C$_5$H$_5$) [R = CF$_3$, 2.05 Å;[10a] R = CO$_2$Me, 2.082 (5) Å[10c]]. In both 4 and 14 the diene is considerably twisted, and thus the two C=C bonds are unable to enter into conjugation, with the result that the C=C double bonds are localized [C(34)–C(33) = 1.362 (4) and 1.346 (6) Å and C(37)–C(38) = 1.382 (5) and 1.370 (6) Å, respectively] while the C—C single bonds [1.478 (4) and 1.484 (6) Å, respectively] are longer than in normal planar 1,3-diene systems.

Conclusion. The present study has confirmed that the reactions between C$_2$(CN)$_4$ and ruthenium σ-acetylide complexes take a similar couse to that found for W(C$_2$Ph)(CO)$_3$(η-C$_5$H$_5$) (Scheme I).[1] In the present case, the nature of the product is determined by other ligands on the metal and particularly with the Ru(PPh$_3$)$_2$(η-C$_5$H$_5$) systems, by the tendency for one PPh$_3$ ligand to be lost in these reactions. This feature results in ready formation of the η^3-cyanocarbon complexes, which can be converted to butadienyl derivatives by addition of other donor ligands. Where such ready ligand dissociation does not occur, isomeric cyclobutenyl and butadienyl complexes can be characterized, analogous to those found in the tungsten system. Structural studies have revealed a marked nonplanarity of the butadienes, which can assume different orientations in solution as a result of restricted rotation.

Experimental Section

General experimental conditions were described in the previous paper. Literature methods were used to make Ru(C$_2$Ph)(L)-

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(11) Cr(CO)$_3$(η-C$_6$H$_6$): B, Rees and P. Coppens, *Acta Crystallogr., Sect. B*, **B29**, 2516 (1973). Mn(CO)$_3$(η-C$_5$H$_5$): P. J. Fitzpatrick, Y. LePage, J. Sedman, and I. S. Butler, *Inorg. Chem.*, **20**, 2852 (1981). Re(CO)$_3$(η-C$_5$H$_5$): P. J. Fitzpatrick, Y. LePage, and I. S. Butler, *Acta Crystallogr., Sect. B*, **B37**, 1052 (1981). Co(CO)$_2$(η-C$_5$H$_5$): B. Beagley, C. R. Parrott, V. Albrecht, and G. G. Young, *J. Mol. Struct.*, **52**, 47 (1979). Co(CO)$_2$(η-C$_5$H$_4$Me): L. R. Byers and L. F. Dahl, *Inorg. Chem.*, **19**, 277 (1980).

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(PPh$_3$)(η-C$_5$H$_5$) [L = CO, PPh$_3$, P(OMe)$_3$],[13] Ru(C$_2$Me)(PPh$_3$)$_2$(η-C$_5$H$_5$),[13] Ru(C$_2$Ph)(dppe)(η-C$_5$H$_5$),[13] and [CH$_2$C$_2$Ru(PPh$_3$)$_2$(η-C$_5$H$_5$)]$_2$.[14]

Reactions of Tetracyanoethylene. (a) With Ru(C$_2$Ph)(PPh$_3$)$_2$(η-C$_5$H$_5$). A mixture of Ru(C$_2$Ph)(PPh$_3$)$_2$(η-C$_5$H$_5$) (1.0 g, 1.26 mmol) and tcne (200 mg, 1.56 mmol) was heated in refluxing benzene (50 mL) for 1.5 h. Chromatography on an alumina column yielded an orange band eluted with dichloromethane, which on crystallization (hexane) gave orange crystals of Ru[η^3-C(CN)$_2$CPhC=C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$) (**3**) (680 mg, 82%): mp >210 °C dec; infrared (Nujol) ν(CN) 2215 (s), ν(C=C) 1590 (s) cm^{-1}, other bands at 1405 (m), 1087 (w), 1080 (m), 1077 (sh), 1068 (w), 1013 (w), 993 (w), 842 (sh), 839 (m), 833 (sh), 829 (w), 802 (w), 765 (m), 753 (m), 742 (m), 698 (s), 692 (s), 689 (m), 660 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.76 (s, 5 H, C$_5$H$_5$), 7.5 (m, 20 H, Ph); ^{13}C NMR (CDCl$_3$) δ 7.3 (d, J(CP) = 6 Hz, C(2)), 66.7 (d, J(CP) = 3 Hz, C(4)), 85.1 (d, J(CP) = 7 Hz, C(1)), 92.3 (s, C$_5$H$_5$), 111.2, 115.9 (2 × d, J(CP) = 3 Hz), 118.7, 119.0 (2 × s, CN), 128.5–134.9 (m, Ph), 218.8 (d, J(CP) = 15 Hz, C(3)). Anal. Calcd for C$_{37}$H$_{25}$N$_4$PRu: C, 67.6; H, 3.8; N, 8.5; M, 658. Found: C, 66.8; H, 3.6; N, 8.3; M (mass spectrometry), 658.

(b) With Ru(C$_2$Me)(PPh$_3$)$_2$(η-C$_5$H$_5$). A mixture of Ru(C$_2$Me)(PPh$_3$)$_2$(η-C$_5$H$_5$) (500 mg, 0.68 mmol) and tcne (90 mg, 0.70 mmol) in benzene (50 mL) was stirred (12 h) and then heated at reflux point (1 h). Elution from an alumina column yielded a major orange band (4:1 dichloromethane/petroleum ether) and a minor unidentified green band (dichloromethane). Crystallization of the major product (dichloromethane/ethanol) yielded orange-red crystals of Ru[η^3-C(CN)$_2$CMeC=C(CN)$_2$](PPh$_3$)(η-C$_5$H$_5$) (**17**) (178 mg, 44%): mp >180 °C dec; infrared (Nujol) ν(CN) 2225 (s), 2219 (sh), ν(C=C) 1615 (s), 1587 (m) cm^{-1}, other bands at 1483 (m), 1440 (s), 1411 (m), 1319 (w), 1311 (w), 1297 (m), 1259 (m), 1189 (m), 1093 (m), 1090 (s), 1052 (w), 1028 (m), 1011 (w), 999 (w), 861 (sh), 857 (m), 842 (s), 827 (m), 796 (s), 759 (s), 750 (m), 705 (sh), 699 (s), 693 (w), 640 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.27 (s, 3 H, Me), 4.79 (s, 5 H, C$_5$H$_5$), 7.5 (m, 15 H, Ph); ^{13}C NMR (CDCl$_3$) δ 11.0 (d, J(CP) = 6 Hz, C(2)), 21.1 (s, Me); 63.1 (d, J(CP) = 3 Hz, C(4)), 82.9 (m, C(1)), 90.5 (s, C$_5$H$_5$), 111.6, 115.6 (2 × d, J(CP) = 3 Hz), 118.0, 118.4 (2 × s, CN), 128.4–136.7 (m, Ph), 218.3 (d, J(CP) = 15 Hz, C(3)). Anal. Calcd for C$_{32}$H$_{23}$N$_4$PRu: C, 64.5; H, 3.8; N, 9.4; M, 596. Found: C, 64.0; H, 3.8; N, 9.4; M (mass spectrometry), 596.

(c) With Ru(PPh$_3$)$_2$(η-C$_5$H$_5$)C$_2$CH$_2$CH$_2$C$_2$Ru(PPh$_3$)$_2$(η-C$_5$H$_5$). (i) Using an Equivalent Amount of tcne. A reaction of the dialkynyl complex (246 mg, 0.17 mmol) and tcne (23 mg, 0.18 mmol) in benzene (35 mL) for 18 h gave a yellow solution. Elution from an alumina column (2:5 dichloromethane/petroleum ether) and crystallization from hexane yielded Ru{η^3-C(CN)$_2$C[CH$_2$CH$_2$C$_2$Ru(PPh$_3$)$_2$(η-C$_5$H$_5$)]C=C(CN)$_2$}(PPh$_3$)(η-C$_5$H$_5$) (**18**) as a yellow powder (141 mg, 63%): mp >160 °C dec; infrared (Nujol) ν(CN) 2210 (s), ν(C≡C) 2100 (s), ν(C=C) 1620 (s), 1587 (m), 1572 (w) cm^{-1}, other bands at 1482 (s), 1446 (s), 1327 (m), 1311 (sh), 1187 (m), 1158 (w), 1090 (s), 1071 (w), 1027 (w), 999 (m), 920 (w (br)), 843 (sh), 834 (m), 819 (w), 804 (m), 746 (s), 696 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.5–3.2 (br, 4 H, CH$_2$), 4.25 (s, 5 H, C$_5$H$_5$ (acetylide)), 4.53 (s, 5 H, C$_5$H$_5$ (allyl)), 7.2–7.5 (m, 45 H, Ph); ^{13}C NMR (CDCl$_3$) δ 10.6 (d, J(CP) = 5 Hz, C(2)), 24.6 (s, ≡C*C*H$_2$), 39.9 (s, C(2)*C*H$_2$), 66.7 (d, J(CP) = 3 Hz, C(4)), 82.0 (d, J(CP) = 7 Hz, C(1)), 84.9 (s, C$_5$H$_5$ (acetylide)), 90.1 (s, C$_5$H$_5$ (allyl)), 98.0 (t, J(CP) = 26 Hz, RuC≡), 108.4 (s, ≡*C*CH$_2$), 112.6 (d, J(CP) = 3 Hz), 116.1 (d, J(CP) = 3 Hz), 118.6 (m, CN), 127.1–140.9 (m, Ph), 219.0 (d, J(CP) = 15 Hz, C(3)). Anal. Calcd for C$_{76}$H$_{59}$N$_4$P$_3$Ru$_2$: C, 69.0; H, 4.5; N, 4.2. Found: C, 69.1; H, 4.9; N, 4.1.

(ii) Using Excess tcne. A reaction of the dialkynyl complex (170 mg, 0.12 mmol) and tcne (50 mg, 0.39 mmol) in benzene (30 mL) gave a yellow solution over 18 h. Elution from an alumina column (4:1 dichloromethane/petroleum ether) yielded a minor unidentified red band and a major yellow band (dichloromethane) which on crystallization from ethanol gave {CH$_2$[η^3-C(CN)$_2$CC=C(CN)$_2$]Ru(PPh$_3$)(η-C$_5$H$_5$)}$_2$ (**19**) as a yellow powder (66 mg, 48%): mp 107–110 °C; infrared (Nujol) ν(CN) 2220 (s), ν(C=C) 1613 (s) cm^{-1}, other bands at 1438 (s), 1412 (w), 1310 (m), 1259 (w), 1187 (w), 1182 (w), 1089 (s), 996 (w), 987 (sh), 845 (m), 822 (w), 755 (sh), 747 (s), 701 (s), 693 (s) 682 (sh) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.2 (m, 4 H, CH$_2$), 4.95 (s, 10 H, C$_5$H$_5$), 7.5 (m, 30 H, Ph); ^{13}C NMR (CDCl$_3$) δ 10.6 (d, J(CP) = 4 Hz, C(2)), 38.5 (s, CH$_2$), 63.6 (s, C(4)), 90.0 (s, C$_5$H$_5$), 114.0–118.6 (m, CN), 128.6–135.0 (m, Ph), C(1) and C(3) were not detected due to low solubility. Anal. Calcd for C$_{64}$H$_{44}$N$_8$P$_2$Ru$_2$: C, 64.6; H, 3.7; N, 9.4. Found: C, 64.3; H, 3.6; N, 9.3.

(d) With Ru(C$_2$Ph)(CO)(PPh$_3$)(η-C$_5$H$_5$). (i) In Diethyl Ether. A reaction of Ru(C$_2$Ph)(CO)(PPh$_3$)(η-C$_5$H$_5$) (100 mg, 0.18 mmol) with tcne (100 mg, 0.78 mmol) in diethyl ether (20 mL) over 5 h resulted in the precipitation of Ru[$\overline{\mathrm{C{=}CPhC(CN)_2C}}(CN)_2$](CO)(PPh$_3$)($\eta$-C$_5H_5$) (**8**) as a yellow powder (112 mg, 91%): mp 124–126 °C; infrared (Nujol) ν(CN) 2218 (w), ν(CO) 1960 (vs), ν(C=C) 1611 (vw), 1572 (vw), 1525 (w) cm^{-1}, other bands at 1184 (w), 1096 (m), 1090 (m), 1072 (w), 999 (m), 838 (m), 819 (m), 752 (m), 744 (m), 697 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.10 (s, 5 H, C$_5$H$_5$), 6.9–7.5 (m, 20 H, Ph). The C$_5$H$_5$ resonance starts to shrink within minutes with growth of a new peak at δ 4.86. After 0.5 h the cyclobutenyl complex **8** all but disappears, while a third peak at δ 5.16 becomes clearly visible. After 12 h the peaks at δ 4.86 and 5.16, due to the isomers of Ru{C[=C(CN)$_2$]CPh=C(CN)$_2$}(CO)(PPh$_3$)(η-C$_5$H$_5$) (**12**), reach an equilibrium where the low-field peak is in slight predominance.

(ii) In Benzene. A reaction of Ru(C$_2$Ph)(CO)(PPh$_3$)(η-C$_5$H$_5$) (250 mg, 0.45 mmol) and tcne (100 mg, 0.78 mmol) in benzene (25 mL) over 24 h led to the precipitation of a yellow powder. Recrystallization (dichloromethane/cyclohexane) gave yellow microcrystals of Ru{C[=C(CN)$_2$]CPh=C(CN)$_2$}(CO)(PPh$_3$)(η-C$_5$H$_5$) (**12**) (280 mg, 91%): mp 208–209 °C; infrared (CH$_2$Cl$_2$) ν(CN) 2226 (m), 2219 (m), 2212 (m), ν(CO) 1949 (vs) cm^{-1}, ν(C=C) (Nujol) 1516 (m) cm^{-1}, other bands at (Nujol) 1303 (w), 1163 (w), 1150 (w), 1082 (m), 990 (w), 830 (m), 816 (m), 750 (w), 743 (w), 732 (m), 724 (w), 691 (sh), 683 (s), 658 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.86 (s, 5 H, C$_5$H$_5$), 7.46 (m, 20 H, Ph) [after 12 h a new C$_5$H$_5$ peak is observed at δ 5.16 (ca. 60%)]; ^{13}C NMR (CDCl$_3$) (the two isomers are separately assigned as A and B; isomer B is the more intense) δ 75.7 (A) (under CDCl$_3$), 76.2 (B, 2 × s, C(1)), 90.3 (A), 90.6 (B, 2 × s, C$_5$H$_5$), 94.0 (B), 95.0 (A, 2 × d, J(CP) = 3 Hz, C(4)), 112.8 (s), 113.6 (d, J(CP) = 4 Hz), 116.9, 117.4 (2 × s, CN), 128.8–135.7 (m, Ph), 181.2 (B), 184.7 (A, 2 × s, C(2)), 204.0 (B), 204.2 (A, 2 × d, J(CP) = 19 Hz, CO), 213.4, 215.6 (2 × d, J(CP) = 12 Hz, C(3)). Anal. Calcd for C$_{38}$H$_{25}$N$_4$OPRu: C, 66.6; H, 3.7; N, 7.9, M, 686. Found: C, 66.7; H, 3.9; N, 8.2; M (mass spectrometry), 686.

(e) With Ru(C$_2$Ph)[P(OMe)$_3$](PPh$_3$)(η-C$_5$H$_5$). (i) In Benzene. Upon mixing Ru(C$_2$Ph)[P(OMe)$_3$](PPh$_3$)(η-C$_5$H$_5$) (460 mg, 0.70 mmol) and tcne (110 mg, 0.86 mmol) in benzene (25 mL) a white powder precipitated. This was identified as Ru[$\overline{\mathrm{C{=}CPhC(CN)_2C}}(CN)_2$][P(OMe)$_3$](PPh$_3$)($\eta$-C$_5H_5$) (**9**) (308 mg, 56%): mp 142–145 °C; infrared (Nujol) ν(CN) 2239 (vw), ν(C=C) 1609 (vw), 1587 (vw), 1568 (w), ν(PO) 1059 (s), 1043 (s), 1011 (m) cm^{-1}, other bands at 1434 (m), 1235 (w), 1183 (w), 1172 (w), 1091 (m), 1001 (w), 991 (sh), 861 (w), 850 (sh), 809 (m), 767 (m), 754 (m), 749 (m), 720 (m), 707 (m), 698 (m), 681 (m), 659 (w) cm^{-1}; ^{1}H NMR δ(CDCl$_3$) 3.44 (d, J(PH) = 11 Hz, 9 H, CH$_3$), 4.70 (d, J(PH) = 1 Hz, 5 H, C$_5$H$_5$), 6.3–7.4 (m, 20 H, Ph). On standing two spectra grow over ca. 15 h: δ 3.50 (d, J(PH) = 11 Hz, CH$_3$), 4.70 (d, J(PH) = 1 Hz, C$_5$H$_5$), 6.7–7.4 (m, Ph); 3.52 (d, J(PH) = 11 Hz, CH$_3$), 4.84 (d, J(PH) = 1 Hz, C$_5$H$_5$), 6.7–7.4 (m, Ph). After leaving for an extended period (16 h, 100 °C) the spectrum of **13**, described below, is present.

(ii) Formation of Ru{C[=C(CN)$_2$]CPh=C(CN)$_2$}[P(OMe)$_3$](PPh$_3$)(η-C$_5$H$_5$) (13). A solution of Ru[$\overline{\mathrm{C{=}CPhC(CN)_2C}}(CN)_2$][P(OMe)$_3$](PPh$_3$)($\eta$-C$_5H_5$) (**9**) (270 mg, 0.35 mmol) in chloroform (30 mL) was heated at reflux point for 17 h. Purification by TLC (silica gel, diethyl ether, R_f ca. 0.4) and recrystallization (dichloromethane/methanol) gave Ru{C[=C(CN)$_2$]CPh=C(CN)$_2$}[P(OMe)$_3$](PPh$_3$)(η-C$_5$H$_5$)·0.25CH$_2$Cl$_2$ (**13**) as red crystals (104 mg, 37%): mp 170–171 °C; infrared (Nujol)

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Table IV. Final Positional (×10⁴) and Thermal Parameters (×10³) for Non-Hydrogen Atoms in $Ru\{C[=C(CN)_2]CPhC=C(CN)_2\}(dppe)(\eta\text{-}C_5H_5)\cdot 0.5CHCl_3$

	x	*y*	*z*	*U*(11)	*U*(22)	*U*(33)	*U*(23)	*U*(13)	*U*(12)
Ru(1)	26798 (3)	6770 (3)	30517 (2)	328 (2)	352 (2)	309 (2)	34 (1)	8 (1)	57 (1)
P(1)	1953 (1)	59 (1)	1645 (1)	31	38 (1)	34 (1)	−2	4	5
P(2)	422 (1)	761 (1)	2865 (1)	35 (1)	39 (1)	35 (1)	3	7	6
C(1)	101 (4)	143 (3)	1248 (3)	31 (2)	50 (2)	38 (2)	−4 (2)	3 (2)	6 (2)
C(2)	−372 (4)	999 (3)	1764 (2)	34 (2)	42 (2)	39 (2)	3 (2)	5 (2)	8 (2)
C(3)	−565 (4)	−561 (3)	2954 (3)	41 (2)	47 (2)	41 (2)	8 (2)	5 (2)	1 (2)
C(4)	−108 (4)	−1543 (4)	2813 (3)	40 (2)	49 (2)	52 (3)	6 (2)	12 (2)	9 (2)
C(5)	−919 (5)	−2552 (4)	2742 (3)	57 (3)	41 (2)	59 (3)	5 (2)	13 (2)	6 (2)
C(6)	−2184 (5)	−2575 (4)	2842 (3)	54 (3)	44 (2)	68 (3)	11 (2)	15 (2)	−2 (2)
C(7)	−2648 (5)	−1590 (4)	3013 (4)	36 (3)	61 (3)	106 (5)	6 (3)	26 (3)	3 (2)
C(8)	−1863 (5)	−594 (4)	3069 (4)	43 (3)	48 (3)	89 (4)	6 (2)	20 (3)	11 (2)
C(9)	−228 (4)	1711 (4)	3481 (3)	43 (2)	50 (2)	47 (2)	−7 (2)	17 (2)	−4 (2)
C(10)	−985 (5)	2542 (4)	3143 (3)	55 (3)	59 (3)	61 (3)	−7 (2)	19 (2)	13 (2)
C(11)	−1444 (6)	3224 (5)	3648 (4)	66 (4)	84 (4)	99 (5)	−22 (4)	27 (3)	22 (3)
C(12)	−1188 (7)	3120 (6)	4474 (5)	81 (4)	94 (5)	106 (5)	−45 (4)	53 (4)	−3 (4)
C(13)	−455 (7)	2277 (6)	4829 (4)	91 (5)	116 (5)	60 (4)	−28 (4)	51 (4)	−32 (4)
C(14)	48 (5)	1565 (5)	4337 (3)	66 (3)	74 (3)	51 (3)	−1 (3)	26 (3)	−3 (3)
C(15)	2191 (4)	−1395 (3)	1485 (3)	46 (2)	40 (2)	40 (2)	−3 (2)	10 (2)	6 (2)
C(16)	1150 (5)	−2219 (4)	1156 (4)	46 (3)	56 (3)	85 (4)	−13 (3)	23 (3)	−1 (2)
C(17)	1413 (6)	−3301 (4)	1106 (5)	73 (4)	41 (3)	132 (6)	−17 (3)	39 (4)	−7 (3)
C(18)	2713 (6)	−3569 (4)	1356 (4)	87 (4)	44 (3)	104 (5)	6 (3)	39 (4)	21 (3)
C(19)	3767 (6)	−2760 (4)	1658 (3)	71 (3)	51 (3)	68 (3)	4 (2)	19 (3)	25 (3)
C(20)	3509 (5)	−1679 (4)	1716 (3)	52 (3)	49 (3)	59 (3)	−6 (2)	10 (2)	7 (2)
C(21)	2525 (4)	687 (3)	790 (3)	34 (2)	51 (2)	37 (2)	−2 (2)	2 (2)	0 (2)
C(22)	3135 (4)	132 (4)	277 (3)	34 (2)	67 (3)	46 (3)	−6 (2)	11 (2)	3 (2)
C(23)	3466 (5)	650 (5)	−386 (3)	43 (3)	97 (4)	49 (3)	−4 (3)	17 (2)	5 (3)
C(24)	3228 (5)	1731 (5)	−533 (3)	62 (3)	97 (5)	44 (3)	12 (3)	17 (2)	−8 (3)
C(25)	2628 (6)	2285 (5)	−32 (3)	73 (3)	63 (3)	55 (3)	15 (3)	11 (3)	2 (3)
C(26)	2273 (5)	1766 (4)	624 (3)	59 (3)	49 (3)	41 (2)	2 (2)	9 (2)	6 (2)
C(27)	3412 (5)	3419 (3)	4115 (3)	53 (3)	38 (2)	41 (2)	−1 (2)	14 (2)	3 (2)
C(28)	4796 (5)	3417 (4)	4450 (3)	57 (3)	43 (2)	49 (3)	−3 (2)	6 (2)	1 (2)
C(29)	5366 (6)	3588 (4)	5298 (3)	75 (4)	55 (3)	52 (3)	−2 (2)	−5 (3)	−3 (3)
C(30)	4571 (8)	3784 (4)	5809 (3)	132 (6)	55 (3)	38 (3)	−4 (2)	9 (3)	−2 (3)
C(31)	3178 (7)	3802 (5)	5478 (4)	106 (5)	71 (4)	51 (3)	−6 (3)	41 (3)	−4 (3)
C(32)	2606 (5)	3617 (4)	4639 (3)	65 (3)	50 (3)	52 (3)	−5 (2)	20 (2)	1 (2)
C(33)	2799 (4)	3219 (3)	3193 (3)	36 (2)	34 (2)	42 (2)	−2 (2)	11 (2)	−1 (2)
C(34)	1935 (4)	3900 (3)	2772 (3)	44 (2)	37 (2)	52 (3)	−2 (2)	8 (2)	8 (2)
C(35)	1603 (5)	4862 (4)	3164 (3)	55 (3)	60 (3)	61 (3)	−4 (3)	4 (2)	21 (2)
N(1)	1343 (6)	5640 (4)	3447 (4)	96 (4)	78 (3)	90 (4)	−22 (3)	−4 (3)	47 (3)
C(36)	1355 (5)	3818 (3)	1889 (3)	52 (3)	35 (2)	60 (3)	−3 (2)	5 (2)	9 (2)
N(2)	883 (5)	3797 (4)	1194 (3)	88 (3)	56 (3)	61 (3)	−1 (2)	−11 (3)	23 (2)
C(37)	3263 (4)	2284 (3)	2800 (2)	36 (2)	37 (2)	31 (2)	1 (2)	1 (2)	6 (2)
C(38)	4299 (4)	2584 (3)	2451 (3)	38 (2)	40 (2)	41 (2)	−2 (2)	6 (2)	4 (2)
C(39)	4802 (5)	3712 (4)	2400 (3)	46 (3)	48 (3)	56 (3)	0 (2)	21 (2)	1 (2)
N(3)	5211 (5)	4616 (4)	2378 (3)	86 (3)	58 (3)	96 (4)	2 (3)	48 (3)	−2 (2)
C(40)	5055 (4)	1781 (4)	2183 (3)	36 (2)	57 (3)	47 (3)	−4 (2)	8 (2)	3 (2)
N(4)	5728 (4)	1192 (4)	2012 (3)	47 (2)	77 (3)	78 (3)	−13 (2)	18 (2)	12 (2)
C(41)	3417 (5)	−869 (4)	3617 (3)	60 (3)	44 (3)	58 (3)	10 (2)	−9 (2)	13 (2)
C(42)	4555 (5)	−168 (4)	3542 (3)	43 (3)	59 (3)	59 (3)	5 (2)	−4 (2)	24 (2)
C(43)	4666 (5)	786 (4)	4037 (3)	43 (3)	52 (3)	53 (3)	7 (2)	−13 (2)	5 (2)
C(44)	3605 (5)	706 (4)	4427 (3)	65 (3)	59 (3)	30 (2)	6 (2)	−4 (2)	16 (2)
C(45)	2828 (5)	−337 (4)	4160 (3)	66 (3)	60 (3)	44 (3)	22 (2)	0 (2)	7 (3)
C(46)	7659 (18)	4302 (16)	870 (21)	77 (11)	106 (13)	349 (38)	90 (18)	87 (17)	45 (10)
Cl (1)	7997 (4)	5001 (3)	1464 (3)	95 (3)	90 (2)	122 (3)	−40 (2)	47 (2)	−14 (2)
Cl(2)	6798 (5)	2902 (3)	766 (3)	150 (4)	78 (2)	109 (3)	0 (2)	25 (3)	−24 (2)
Cl(3)	5699 (14)	4570 (17)	177 (11)	277 (16)	621 (31)	367 (19)	−220 (21)	224 (17)	−131 (19)

ν(CN) 2248 (vw), 2225 (w), 2212 (m), 2202 (w), ν(C═C) 1525 (m), ν(PO) 1050 (s), 1047 (s), 1042 (sh) cm^{-1}, other bands at 1432 (s), 1265 (m), 1188 (m), 1181 (m), 1175 (m), 1160 (w), 1088 (m), 1000 (w), 920 (w), 912 (w), 838 (w), 825 (w), 817 (m), 780 (m), 770 (m), 756 (sh), 749 (s), 736 (m), 722 (s), 703 (m), 699 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.50 (d, *J*(PH) = 11 Hz, 9 H, CH_3), 4.69 (d, *J*(PH) = 1 Hz, 5 H, C_5H_5), 5.30 (s, 0.5 H, CH_2Cl_2), 6.7–7.6 (m, 20 H, Ph); ^{13}C NMR ($CDCl_3$) δ 53.6 (d, *J*(CP) = 12 Hz, CH_3), 86.6 (s, C_5H_5), 97.4 (m, C(4)), 113.9, 114.5, 119.1 (3 × s, CN), 128.2–133.8 (m, Ph), 177.2 (m, C(2)), 223.6 (d, *J*(CP) = 15 Hz, C(3)) [C(1) is obscured by $CDCl_3$ peaks]. Anal. Calcd for $C_{40}H_{34}N_4O_3P_2Ru\cdot 0.25CH_2Cl_2$: C, 60.2; H, 4.3; N, 7.0; *M*, 782. Found: C, 59.8; H, 4.8; N, 6.7; *M*(mass spectrometry), 782.

(f) With $Ru(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$. (i) In Benzene. Reaction of a mixture of $Ru(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$ (600 mg, 0.90 mmol) and tcne (136 mg, 1.06 mmol) in benzene (25 mL) for 3 h yielded $Ru[\overline{C{=}CPhC(CN)_2C}(CN)_2](dppe)(\eta\text{-}C_5H_5)$ (**10**) (632 mg, 88%) as a yellow powder. Rapid recrystallization (dichloromethane/ethanol) gave $Ru[\overline{C{=}CPhC(CN)_2C}(CN)_2](dppe)(\eta\text{-}C_5H_5)\cdot 0.25CH_2Cl_2$ in a microcrystalline form: mp >170 °C dec; infrared (Nujol) ν(CN) 2235 (vw), 2210 (vw (br)), ν(C═C) 1545 (w) cm^{-1} other bands at 1437 (m), 1311 (w), 1228 (sh), 1223 (w), 1100 (m), 1000 (m), 859 (w), 851 (w), 845 (sh), 811 (m), 758 (sh), 749 (m), 744 (m), 712 (m), 701 (s), 668 (m), 659 (w), 645 (sh) cm^{-1}; ^{1}H NMR: ($CDCl_3$) δ 1.5–2.6 (m, 4 H, CH_2), 4.66, 4.99 (2 × s, 5 H, C_5H_5), 5.29 (s, 0.5 H, CH_2Cl_2), 7.0–7.9 (m, Ph) [after 12 h the spectrum of **10** had all but disappeared, while peaks due to **14**, described below, had formed]; ^{13}C NMR ($CDCl_3$) δ 25.0 (m, CH_2), 85.6 (s, C_5H_5), 127.6–146.3 (m, Ph), other resonances could not be observed before **14** had formed. Anal. Calcd for $C_{45}H_{34}N_4P_2Ru\cdot 0.25CH_2Cl_2$: C, 66.7; H, 4.3; N, 6.9. Found: C, 67.2; H, 4.3; N, 7.0.

(ii) Formation of $Ru\{C[=C(CN)_2]CPh=C(CN)_2\}(dppe)(\eta\text{-}C_5H_5)$ (14). After $Ru(C_2Ph)(dppe)(\eta\text{-}C_5H_5)$ (300 mg, 0.45 mmol) was reacted with tcne (60 mg, 0.47 mmol) in benzene (25 mL) for

6 h, the cyclobutenyl product **13** was collected and dissolved in chloroform (25 mL). Upon standing for 7 days, precipitation with ethanol and recrystallization (dichloromethane/methanol) gave red crystals of Ru{C[=C(CN)$_2$]CPh=C(CN)$_2$}(dppe)(η-C_5H_5)·CH_2Cl_2 (**14**) (329 mg, 83%): mp 212–214 °C; infrared (Nujol) ν(CN) 2219 (w), 2208 (w), 2199 (w), ν(C=C) 1520 (m) cm^{-1}, other bands at 1088 (m), 870 (w), 813 (sh), 802 (m), 763 (m), 747 (s), 737 (m), 700 (s), 692 (m), 671 (w), 652 (sh) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.2–2.2 (m, 4 H, CH_2), 4.13, 5.04 (2 × s, 5 H, C_5H_5), 5.29 (s, 2 H, CH_2Cl_2), 6.2–7.8 (m, 25 H, Ph); ^{13}C NMR ($CDCl_3$) δ 24.2–27.7 (m, CH_2), 53.5 (s, CH_2Cl_2), 73.9 (m, C(1)), 86.3, 86.9 (2 × s, C_5H_5), 95.1 (m, C(4)), 113.8, 114.6, 118.1, 119.4 (4 × s, CN), 128.6–144.8 (m, Ph), 181.9 (m, C(2)), 225.7 (m, C(3)). Anal. Calcd for $C_{45}H_{34}N_4P_2Ru{\cdot}CH_2Cl_2$: C, 62.9; H, 4.1; N, 6.4; *M*, 794. Found: C, 61.9; H, 4.0; N, 6.3; *M* (mass spectrometry), 794.

Reaction of Ru[η^3-C(CN)$_2$CPhC=C(CN)$_2$](PPh$_3$)(η-C_5H_5) (3) with CO. A solution of complex **3** (130 mg, 0.20 mmol) in tetrahydrofuran (50 mL) was carbonylated in an autoclave (53 atm of CO, 120 °C, 17 h). The yellow solution was taken to dryness, extracted with diethyl ether, and crystallized from cyclohexane. Recrystallization (dichloromethane/cyclohexane) gave yellow microcrystals of Ru{C[=C(CN)$_2$]CPh=C(CN)$_2$}(CO)(PPh$_3$)(η-C_5H_5) (**12**) (120 mg, 89%). This was identified by comparing its infrared and NMR spectra with those of the fully characterized complex, described above. In the ^{1}H NMR spectrum both isomers were present initially in solution.

Reaction of Ru[η^3-C(CN)$_2$CPhC=C(CN)$_2$](PPh$_3$)(η-C_5H_5) (3) with CN-*t*-Bu. (a) Under Mild Conditions. A mixture of **3** (140 mg, 0.21 mmol) and CN-*t*-Bu (200 mg, 2.4 mmol) in THF (50 mL) was heated in a 100-mL autoclave under nitrogen (50 atm, 70 °C, 17 h). Filtration, crystallization from cyclohexane, and recrystallization (dichloromethane/cyclohexane) yielded dark red crystals of Ru{C[=C(CN)$_2$]CPh=C(CN)$_2$}(CN-*t*-Bu)(PPh$_3$)(η-C_5H_5) (**4**) (140 mg, 89%): mp 231–233 °C; infrared (CH_2Cl_2) ν(CN) 2224 (m), 2216 (m), 2209 (m), ν(CN-*t*-Bu) 2138 (s), ν(C=C) (Nujol) 1510 (m), 1503 (sh); other bands at 1301 (w), 1254 (w), 1224 (w), 1202 (m), 1096 (m), 1078 (m), 1062 (w), 991 (w), 828 (m), 812 (sh), 803 (m), 748 (m), 740 (m), 733 (m), 714 (m), 688 (s), 679 (sh), 659 (m), 652 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.33 s, 9 H, Me), 4.62 (s, 5 H, C_5H_5), 7.4 (m, 20 H, Ph); upon warming two new singlets appeared at δ 1.26 (Me) and 4.54 (C_5H_5) accounting for about 30% of the protons; ^{13}C NMR ($CDCl_3$) δ 30.5 (s, Me), 58.1 (s, *tert*-C), 73.8 (s, C(1)), 86.7, 87.0 (2 × s (ratio = 1:2.5), C_5H_5), 95.2 (s, C(4)), 113.4, 114.1, 114.5, 118.4 (4 × s, CN), 128.9–136.7 (m, Ph), 151.7 (s, br, RuCN), 178.1 (s, C(2)), 224.3 (d, *J*(CP) = 9 Hz, C(3)). Anal. Calcd for $C_{42}H_{34}N_5PRu$: C, 68.1; H, 4.6; N, 9.5; *M*, 741. Found: C, 67.6; H, 4.6; N, 9.2; *M* (mass spectrometry), 741.

(b) Under Vigorous Conditions. A mixture of **3** (200 mg, 0.30 mmol) and CN-*t*-Bu (150 mg, 1.8 mmol) in benzene (50 mL) was heated in a 100-mL autoclave under nitrogen (50 atm, 150 °C, 10 h). Reduction to dryness and extraction with petroleum ether (2 × 20 mL) left a yellow residue which on crystallization (dichloromethane/hexane) gave yellow crystals of Ru{C[=C(CN)$_2$]CPh=C(CN)$_2$}(CN-*t*-Bu)$_2$(η-C_5H_5) (**21**) (159 mg, 93%): mp 205–207 °C; infrared (CH_2Cl_2) ν(CN) 2223 (m), 2216 (sh), ν(CN-*t*-Bu) 2162 (s), 2118 (s), ν(C=C) (Nujol) 1530 (m) cm^{-1}, other bands at 1286 (w), 1231 (m), 1228 (sh), 1195 (s), 1005 (w), 988 (w), 831 (w), 802 (m), 768 (w), 738 (w), 692 (m), 659 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.51, 1.61 (2 × s, 18 H, Me), 4.57 (s, 5 H, C_5H_5), 7.49 (s, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 30.7, 31.4 (2 × s, Me), 58.2, 58.4 (2 × s, *tert*-C), 69.3 (s, C(1)), 84.6 (s, C_5H_5), 90.8 (s, C(4)), 113.0, 113.3. 114.1, 117.6 (4 × s, CN), 128.0, 129.0, 131.8, 133.1 (4 × s, Ph), 152.3 (s, RuCN), 179.7 (s, C(2)), 226.2 (s, C(3)). Anal. Calcd for $C_{29}H_{28}N_6Ru$: C, 62.0; H, 5.0; N, 15.0; *M*, 562. Found: C, 62.0; H, 5.1; N, 15.0; *M* (mass spectrometry), 562.

Irradiation of Ru[η^3-C(CN)$_2$CPh=C(CN)$_2$}(CO)(PPh$_3$)(η-C_5H_5) (12). A solution of **12** (150 mg, 0.22 mmol) in 1,2-dimethoxyethane (50 mL) was irradiated for 2 h (Pen-ray high-pressure mercury lamp, 50 W). The volume was reduced to 15 mL and petroleum ether added to give orange crystals of Ru[η^3-C(CN)$_2$CPhC=C(CN)$_2$](PPh$_3$)(η-C_5H_5) (**3**) (100 mg, 70%), identified by comparison with an authentic sample.

ESR Spectra. The ESR spectra of Ru(C_2R)(PPh$_3$)$_2$(η-C_5H_5) (R = Ph or Me) and Ru(C_2Ph)(dppe)(η-C_5H_5) were obtained by using the same conditions as those described in the previous paper.[1]

Crystal Structure of Ru{C[=C(CN)$_2$]CPh=C(CN)$_2$}(dppe)(η-C_5H_5)·0.5CHCl$_3$ (14). A crystal formed as a red diamond, 0.25 × 0.18 × 0.15 mm, was mounted on a glass fiber with epoxy resin. Lattice parameters at 21 °C were determined by a least-squares fit to the setting angles of 25 independent reflections ($\theta < 10°$) measured and refined on an Enraf-Nonius CAD-4 four-circle diffractometer employing graphite-monochromated Mo Kα radiation.

Crystal Data: $C_{45}H_{35}N_4P_2Ru{\cdot}0.5CHCl_3$; formula weight 854.5; triclinic, space group $P\bar{1}$; $a = 10.323$ (5) Å, $b = 12.157$ (8) Å, $c = 16.64$ (1) Å, $\alpha = 91.12$ (6)°, $\beta = 105.55$ (4)°, $\gamma = 95.93$ (5)°; $Z = 2$, $D_{\text{measd}} = 1.44$ (2) g cm^{-3}, D_{calcd} 1.420 g cm^{-3}; $U = 1998.0$ Å^3, $F(000) = 872$ electrons; λ(Mo Kα) = 0.7107 Å; μ(Mo Kα) = 5.62 cm^{-1}.

Intensity data were collected in the range 1.5° < θ < 25° using a ω–2θ scan mode. The ω scan angles and horizontal counter apertures employed were (1.00 + 0.35 tan θ)° and (2.40 + 0.50 tan θ) mm, respectively. Two standard reflections, monitored after every 60 min of data collection, indicated that no decomposition had occurred. Data reduction was performed by using program SUSCAD,[15] which also applied Lorentz and polarization corrections. Of the 6335 reflections collected, 4290 with $I > 2.5\sigma(I)$ were considered "observed" and used in the calculations.

Solution and Refinement of the Structure. The structure was solved by heavy-atom methods; the position of the ruthenium atom was determined from a Patterson map and was then used to phase a Fourier map which revealed all other non-hydrogen atoms. Hydrogen atoms were included at sites calculated assuming planar geometries about phenyl rings and tetrahedral geometries about all other carbons, with fixed bond lengths (C–H = 0.97 Å).

Refinements of positional and anisotropic thermal parameters for the non-hydrogen atoms, group thermal parameters for the hydrogen atoms, and an overall scale factor were performed by a block-matrix least-squares technique. A weighting scheme was also applied and refined and converged at $w = 0.92/(\sigma^2(F_o) + 0.0013F_o^2)$. Refinement converged (all shifts <0.5σ) with $R = 0.036$ and $R_w = 0.039$.[15] The larger peaks in the final difference map were found near the $CHCl_3$ molecule; all were <0.7 e Å^{-3} and were between 0.3 and 0.8 Å from C(46) or Cl(3).

All calculations were performed by using the SHELX[16] system of programs, and all scattering factors (neutral Ru) and anomalous dispersion terms were taken from ref 17. The final positional and thermal parameters for non-hydrogen atoms are listed in Table IV; supplementary material deposited contains tables of hydrogen atom positional and thermal parameters and a full listing of bond lengths and angles.

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Supplementary Material Available: Tables of hydrogen atom positional and thermal parameters, bond lengths and angles, and observed and calculated structure factors for Ru{C[=C(CN)$_2$]CPh=C(CN)$_2$}(dppe)(η-C_5H_5)·0.5CHCl$_3$ (14) (27 pages). Ordering information is given on any current masthead page.

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(15) The function minimized was $\sum w|F_o - F_c|^2$, $R = \sum(|F_o| - |F_c|)/\sum|F_o|$, and $R_w = \sum(|F_o| - |F_c|)w^{1/2}/\sum(|F_o|w^{1/2})$.

(16) Programs used in this determination included: SUSCAD, data reduction program for the CAD-4 diffractometer, University of Sydney, 1976; SHELX 76, program for crystal structure determination, G. M. Sheldrick, University of Cambridge, 1976; ORTEP, C. K. Johnson, 1965.

(17) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99.