Fractional atomic coordinates and U_{eq}'s are given in Table IV.

Acknowledgment. We acknowledge the help and advice of Bill Croasmun, the use of the Southern California Regional NMR Facility, and the support of the NSF Grant No. 7916324A1. We also thank Richard E. Marsh and William P. Schaefer for sage counsel and Sten Samson for his help in the development and improvement of our X-ray diffraction facility. This work has been supported by the National Science Foundation Grant No. CHE8024869.

Registry No. 1, 80964-80-3; 2, 80964-82-5; 3, 84849-47-8; 4, 80964-84-7; 5, 80964-83-6; 6, 84849-48-9; 7, 84849-49-0; $Cp^*TaMe_3(OCMe_3)$, 84849-50-3; Cp^*TaMe_3Cl, 69302-75-6; $KOCMe_3$, 865-47-4.

Supplementary Material Available: Listings of fractional atomic coordinates for hydrogen atoms (Table V), anisotropic Gaussian amplitudes for nonhydrogen atoms (Table VI), and structure factor amplitudes (Table VII) and a stereoscopic drawing of a unit cell of $Cp^*Ta(PMe_3)_2H_4$ (**1**) (Figure 9) (23 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Sheffield, Sheffield S3 7HF, England

Comparison of the Crystal and Molecular Structures of Cyclopentadienylbromodicarbonylruthenium(II) and (Ethyltetramethylcyclopentadienyl)bromodicarbonylruthenium(II)

HARRY ADAMS, NEIL A. BAILEY,* and COLIN WHITE*

Received July 9, 1982

The crystal structures of $\mathrm{Ru}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2\mathrm{Br}$ (monoclinic, $a = 9.807$ (7) Å, $b = 7.023$ (3) Å, $c = 13.436$ (11) Å, $\beta = 106.83$ (6)°, $Z = 4$, $P2_1/c$, $R = 0.0462$) and $\mathrm{Ru}(\eta\text{-}\mathrm{C_5Me_4Et})(\mathrm{CO})_2\mathrm{Br}$ (monoclinic, $a = 6.980$ (6) Å, $b = 11.419$ (9) Å, $c = 9.205$ (8) Å, $\beta = 95.32$ (7)°, $Z = 2$, $P2_1/m$, $R = 0.0460$) show that the molecules adopt rotationally different conformations but otherwise exhibit similar bond lengths for their common skeleton. The former has an ordered, delocalized cyclopentadienyl ring positioned so that one carbon atom closely eclipses the bromo ligand. In contrast, the latter molecule, which has crystallographically imposed C_s symmetry, adopts a staggered conformation with the ring carbon carrying the ethyl substituent trans with respect to the bromide; partial bond localization was also observed within the alkylated ring. A possible relationship between the structural differences and the different reactivities of these two compounds is commented upon.

Introduction

The chemistry of cyclopentadienyl–metal complexes is one of the cornerstones of organometallic chemistry. Over the last 15 years, however, chemists have turned in increasing numbers to the use of pentaalkyl-substituted cyclopentadienyl ligands, which display several desirable features compared to their unsubstituted cyclopentadienyl analogues. For example, they normally exhibit considerably longer catalytic lifetimes as is the case for the oligomerization catalysts $[\mathrm{Y}(\eta^5\text{-}\mathrm{C_5Me_4Et})_2\text{-}n\text{-}\mathrm{Bu}]$[1] and $[\mathrm{Ta}(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Cl_2}(1\text{-octene})]$.[2] In addition, the chemical reactivity is often very different from that of the corresponding cyclopentadienyl complexes; thus, $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C_5Me_5})_2]$ readily reacts with hydrogen or carbon monoxide but $[\mathrm{Mo}(\mathrm{C_5H_5})_2]_n$ is relatively inert.[3] Similarly, whereas the protonated form of the duroquinone complex $[\mathrm{Co}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^4\text{-}\mathrm{C_6Me_4O_2})]$ has only been observed in strong acid solution, the corresponding protonated complex $[\mathrm{Co}(\eta^5\text{-}\mathrm{C_5Me_5})(\eta^6\text{-}\mathrm{C_6Me_4(OH)_2})](\mathrm{BF_4})_2$ may be isolated.[4]

Comparative chemical and structural studies on related compounds have proved to be invaluable in advancing chemical knowledge. For example, such studies on the various effects of changing the nature of the substituents on phosphorus donor ligands have contributed significantly to an understanding of organometallic reactions.[5] Unfortunately, there have been few systematic attempts to compare the structures and properties of peralkyl-substituted and unsubstituted cyclopentadienyl complexes. Obviously peralkyl-substituted cyclopentadienyl ligands are larger and better electron donors than C_5H_5 ligands, but to what extent these features influence the properties of particular metal complexes remains largely a matter of chemical intuition. As a contribution to understanding such factors we report and compare the crystal structures of $\mathrm{Ru}(\mathrm{Cp'})(\mathrm{CO})_2\mathrm{Br}$ (Ia, Cp′ = C_5H_5; Ib, Cp′ = C_5Me_4Et). These two complexes were chosen for comparison because they exhibit distinct differences in their chemical properties. Thus, unlike the C_5H_5 analogue, $\mathrm{Ru}(\eta^5\text{-}\mathrm{C_5Me_4Et})(\mathrm{CO})_2\mathrm{Br}$ is oxidized by bromine to the corresponding ruthenium(IV) complex, $\mathrm{Ru}(\eta^5\text{-}\mathrm{C_5Me_4Et})(\mathrm{CO})\mathrm{Br_3}$.[6] Equally important is the fact that the relative reactivities of these two

Table I. Atomic Positional Parameters with Estimated Standard Deviations for $\mathrm{Ru(C_5H_5)(CO)_2Br}$

	x/a	y/b	z/c
Ru(1)	0.24295 (12)	0.02824 (18)	0.22844 (8)
Br(1)	0.19798 (21)	0.37325 (28)	0.17290 (14)
O(1)	0.3736 (13)	−0.0500 (20)	0.0557 (8)
O(11)	−0.0495 (13)	−0.0853 (22)	0.0941 (8)
C(1)	0.3228 (15)	−0.0190 (26)	0.1182 (11)
C(2)	0.3823 (22)	−0.1644 (30)	0.3365 (11)
C(3)	0.4353 (16)	0.0163 (32)	0.3669 (11)
C(4)	0.3338 (19)	0.1123 (28)	0.3969 (10)
C(11)	0.0631 (16)	−0.0349 (28)	0.1442 (11)
C(12)	0.2470 (24)	−0.1850 (29)	0.3507 (13)
C(13)	0.2153 (19)	−0.0136 (32)	0.3859 (11)

---

[1] D. G. Ballard, A. Courtis, J. Holton, J. McMeeking, and R. Pearce, *J. Chem. Soc., Chem. Commun.*, 994 (1978).
[2] S. J. McLain, J. Sancho, and R. R. Schrock, *J. Am. Chem. Soc.*, **101**, 5451 (1979).
[3] J. L. Thomas, *J. Am. Chem. Soc.*, **95**, 1838 (1973).
[4] G. Fairhurst and C. White, *J. Chem. Soc., Dalton Trans.*, 1531 (1979).
[5] C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977).
[6] I. W. Nowell, K. Tabatabaian, and C. White, *J. Chem. Soc., Chem. Commun.*, 547 (1979).

Table II. Atomic Positional Parameters with Estimated Standard Deviations for $Ru(C_5Me_4Et)(CO)_2Br$[a]

	x/a	*y/b*	*z/c*
Ru(1)	−0.0646 (2)	0.25000	0.19976 (17)
Br(1)	−0.2246 (3)	0.25000	−0.06001 (22)
O(1)	−0.3196 (15)	0.0585 (10)	0.2962 (12)
C(1)	−0.2323 (18)	0.1328 (13)	0.2590 (14)
C(2)	0.2188 (15)	0.1863 (10)	0.1341 (13)
C(3)	0.2022 (15)	0.1483 (10)	0.2735 (13)
C(4)	0.1785 (25)	0.2500	0.3643 (19)
C(5)	0.2498 (19)	0.1117 (12)	0.0021 (15)
C(6)	0.2093 (19)	0.0228 (12)	0.3275 (15)
C(7)	0.1861 (29)	0.2500	0.5302 (20)
C(8)	0.3952 (28)	0.2500	0.5979 (22)

[a] Parameters constrained by the mirror symmetry are reported without estimated standard deviations.

complexes have been quantified by kinetic studies of reaction 1. At 100 °C in diglyme Ib undergoes this reaction at a rate that is more than 18 times that of the unsubstituted cyclopentadienyl complex Ia.[7]

$$Ru(Cp')(CO)_2Br + P(OPh)_3 \rightarrow Ru(Cp')(CO)(P(OPh)_3)Br + CO \quad (1)$$

Experimental Section

$Ru(C_5H_5)(CO)_2Br$.[8] Crystal data: $C_7H_5BrO_2Ru$; M_r = 302.02; crystallization from hexane as very thin, elongated, yellow-brown plates; crystal dimensions 0.57 × 0.17 × 0.01 mm; monoclinic; a = 9.807 (7), b = 7.023 (3), c = 13.436 (11) Å; β = 106.83 (6)°, V = 885.8 (11) Å^3; D_m = 2.24, D_c = 2.265 g cm^{-3}; Z = 4; space group $P2_1/c$ (No. 14, C_{2h}^5); Mo Kα radiation (λ = 0.71069 Å); μ(Mo Kα) = 61.5 cm^{-1}; $F(000)$ = 568.

Data Collection and Refinement. Three-dimensional X-ray diffraction data were collected in the range $6.5 < 2\theta < 50°$ on a Stoe Stadi-2 two-circle diffractometer by the ω-scan method. The 850 independent reflections (1490 total) for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarization effects and for absorption (transmission coefficient range 0.94–0.35); a correction was made for 13% intensity loss during data collection, on the basis of the monitoring of two reflections. The structure was solved by standard Patterson and Fourier methods and refined by block-diagonal least squares. Hydrogen atoms were placed in calculated positions (C–H 0.97 Å); their contributions were included in structure factor calculations (B = 10 Å^2), but no refinement of positional parameters was permitted. Refinement converged at R = 0.0462 ($R = \sum||F_{hkl}^{\text{obsd}}| - k|F_{hkl}^{\text{calcd}}||/\sum|F_{hkl}^{\text{obsd}}|$) with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of ruthenium and bromine. Table I lists the atomic positional parameters with estimated standard deviations.

$Ru(C_5Me_4Et)(CO)_2Br$.[6] Crystal data: $C_{13}H_{17}BrO_2Ru$; M_r = 386.18; crystallization from hexane as elongated, yellow plates; crystal dimensions 0.61 × 0.39 × 0.11 mm; monoclinic; a = 6.980 (6), b = 11.419 (9), c = 9.205 (8) Å; β = 95.32 (7)°, V = 730.5 (15) Å^3, D_m = 1.72, D_c = 1.756 g cm^{-3}; Z = 2; space group $P2_1/m$ (No. 11, (C_{2h}^2); Mo Kα radiation (λ = 0.71069 Å); μ(Mo Kα) = 37.51 cm^{-1}; $F(000)$ = 380.

Data Collection and Refinement. The data were collected ($3.5 < 2\theta < 50°$ on a Nicolet/Syntex R3 diffractometer) and processed (703 independent reflections, 1229 total, absorption corrections not applied), and the structure was solved and refined (R = 0.0460) as for the analogous cyclopentadienyl complex above (no crystal decay was detected). The hydrogen atoms were detected and included in structure factor calculations in calculated positions (C–H 0.96 Å, C–C–H (methyl) 111°, B = 8.0 Å^2); those attached to the methyl carbon of the ethyl group were clearly detected to be disordered, essentially equally, between six sites around the annulus in a manner that was consistent with the presence of two mirror symmetry related conformations of the ethyl group in the crystal lattice. Table II lists atomic positional parameters and estimated standard deviations.

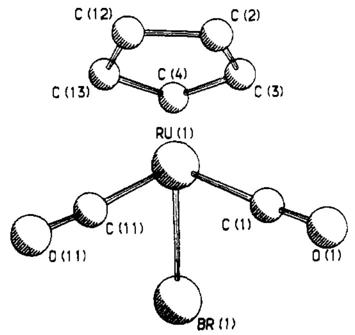

Figure 1. Molecular structure of $Ru(C_5H_5)(CO)_2Br$ showing the approximate mirror plane that relates atoms C(2) and C(12) etc.

Table III. Bond Lengths (Å) and Bond Angles (deg) with Estimated Standard Deviations in Parentheses for Both Molecules

	$[Ru(C_5H_5)(CO)_2Br]$	$[Ru(C_5Me_4Et)(CO)_2Br]$
Ru(1)–Br(1)	2.536 (2)	2.544 (2)
Ru(1)–C(1)	1.895 (16)	1.892 (14)
Ru(1)–C(11)	1.853 (17)	
Ru(1)–C(2)	2.158 (20)	2.242 (11)
Ru(1)–C(3)	2.235 (18)	2.246 (12)
Ru(1)–C(4)	2.258 (18)	2.167 (14)
Ru(1)–C(12)	2.214 (20)	
Ru(1)–C(13)	2.230 (19)	
C(1)–O(1)	1.114 (20)	1.116 (17)
C(11)–O(11)	1.169 (21)	
C(2)–C(12)	1.40 (3)	1.455 (16) (C(2)–C(2′))
C(2)–C(3)	1.39 (3)	1.370 (16)
C(3)–C(4)	1.36 (3)	1.449 (18)
C(4)–C(13)	1.43 (3)	
C(12)–C(13)	1.36 (3)	
		1.516 (18) (C(2)–C(5))
		1.516 (18) (C(3)–C(6))
		1.523 (21) (C(4)–C(7))
		1.533 (23) (C(7)–C(8))
Br(1)–Ru(1)–C(1)	90.8 (5)	92.4 (4)
Br(1)–Ru(1)–C(11)	89.7 (5)	
C(1)–Ru(1)–C(11)	91.0 (7)	90.1 (5) (C(1)–Ru(1)–C(1′))
Ru(1)–C(1)–O(1)	177.5 (14)	174.8 (11)
Ru(1)–C(11)–O(11)	175.9 (15)	
C(12)–C(2)–C(3)	110.1 (17)	108.5 (9) (C(2′)–C(2)–C(3))
C(2)–C(3)–C(4)	107.3 (16)	108.1 (10)
C(3)–C(4)–C(13)	107.8 (16)	106.5 (11) (C(3)–C(4)–C(3′))
C(13)–C(12)–C(2)	106.1 (18)	
C(4)–C(13)–C(12)	108.7 (17)	
		127.1 (11) (C(3)–C(2)–C(5))
		124.2 (9) (C(2′)–C(2)–C(5))
		127.1 (11) (C(2)–C(3)–C(6))
		124.8 (11) (C(4)–C(3)–C(6))
		125.7 (12) (C(3)–C(4)–C(7))
		110.6 (12) (C(4)–C(7)–C(8))

Tables of anisotropic thermal vibrational parameters with estimated standard deviations, predicted hydrogen atom positional parameters, and observed structure amplitudes and calculated structure factors are deposited in the supplementary material. Scattering factors were taken from ref 9. Following unit weight refinements, no anomalies were detected in agreement analyses and, in view of the recognized limitations of the two data sets, it was considered that the use of more elaborate schemes of weights would be unjustified. The computer programs used formed part of a suite of programs written and developed in Sheffield for use on the Sheffield University ICL 1906S computer. Further details are available from the authors.

Results and Discussion

The structures of the two molecules are illustrated in Figures 1 and 2, in each case with the atom labeling used in the corresponding tables. Bond lengths and angles are compared

---

(7) K. Tabatabaian and C. White, *Inorg. Chem.*, **20**, 2020 (1981).

(8) R. J. Haines and A. L. du Preez, *J. Chem. Soc., Dalton Trans.*, 944 (1972).

(9) "International Tables for X-ray Crystallography", Vol. 4, Kynoch Press, Birmingham, England, 1974.

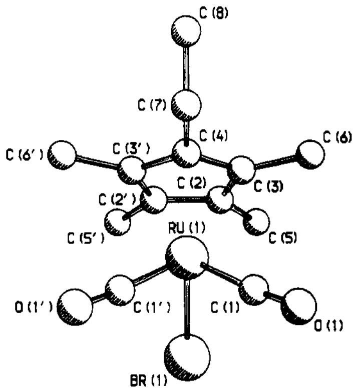

Figure 2. Molecular structure of $Ru(C_5Me_4Et)(CO)_2Br$ showing the crystallographically imposed mirror symmetry. Atoms labeled with a prime are symmetry related to those similarly labeled without the prime.

Table IV. Details of Planar Fragments of the Two Molecules[a]

p	*q*	*r*	*d*
(a) $[Ru(C_5H_5)(CO)_2Br]$			
Plane: C(2)–C(4), C(12), C(13)			
0.1396	−0.3180	0.9378	4.7777
(C(2) −0.012, C(3) 0.007, C(4) 0.000, C(12) 0.012, C(13) −0.008, Ru(1) −1.877)			
(b) $[Ru(C_5Me_4Et)(CO)_2Br]$			
Plane A: C(2), C(3), C(2'), C(3')			
0.9836	0.0000	0.1804	1.6112
(Ru(1) −1.892, C(4) −0.089, C(5) 0.106, C(6) 0.093, C(7) 0.098, C(8) 1.589)			
Plane B: C(3), C(4), C(3')			
0.9597	0.0000	0.2809	1.8350
(Ru(1) −1.917, C(2) −0.134, C(6) 0.142, C(7) 0.343, C(8) 1.862)			
Angle between Planes A and B 5.9°			

[a] Equations of the mean planes are of the form $px + qy + rz = d$, where *p*, *q*, and *r* are direction cosines referred to orthogonal axes *a*, *b*, *c**; deviations of atoms (Å) from the mean planes are given in parentheses.

in Table III; details of planar fragments of both molecules are given in Table IV.

The structure of $Ru(C_5Me_4Et)(CO)_2Br$ has crystallographically imposed mirror symmetry; that of $Ru(C_5H_5)(CO)_2Br$ has approximate mirror symmetry. In both compounds the $Ru(CO)_2Br$ fragments are very similar and conventional in geometry. It is noteworthy that the Ru–carbonyl distances are not significantly different although the ethyltetramethylcyclopentadienyl ligand is a more electron-rich ligand than cyclopentadienyl and also despite the fact that differences are observed in the carbonyl stretching frequencies (IR (diglyme): $Ru(C_5Me_4Et)(CO)_2Br$, $\nu(CO)$ 2026 and 1967 cm^{-1}; $Ru(C_5H_5)(CO)_2Br$, $\nu(CO)$ 2052 and 1987 cm^{-1}). This appears to be a general result since similar bond distances were noted for $[M(C_5R^1{}_4R^2)(CO)_2]_2$ (M = Fe, $R^1 = R^2 = H$[10a] or Me;[10b] M = Ru, $R^1 = R^2 = H$,[11a] R^1 = Me, R^2 = Et[11b]) and $[Cr(C_5R_5)(CO)_2NO]$ (R = H[12a] or Me[12b]). Significant shortening of metal–carbonyl bond lengths has been observed when two peralkylcyclopentadienyl ligands are present, e.g., $Zr(C_5R_5)_2(CO)_2$: R = H, Zr–CO = 2.187 (4) Å;[13a] R = Me, Zr–CO = 2.145 (4) Å.[13b]

In $Ru(C_5H_5)(CO)_2Br$ the cyclopentadienyl ring is planar, essentially regularly delocalized, and bonded in such a way that the carbon atom lying in the approximate molecular mirror plane lies above (i.e., approximately eclipses) the bromo ligand. The ring in the alkylated complex is less perfectly planar with a "hinge" about the C(3)···C(3') line such that atom C(4) bends *toward* the ruthenium atom. The orientation of the pentaalkylcyclopentadienyl ring is such that the unique carbon atom carrying the ethyl substituent is opposite to (i.e., is staggered with respect to) the bromo ligand in contrast to the eclipsed orientation in $Ru(C_5H_5)(CO)_2Br$. As observed in other peralkylcyclopentadienyl compounds,[10b,11b,14a–c] the alkyl substituents are all displaced away from the metal; evidence indicates that this is due to electronic rather than steric factors.[12b,15] In both structures, the carbon atoms of the cyclopentadienyl rings which are most nearly trans to the bromo ligand are nearer to the ruthenium, suggesting a greater degree of π-back-bonding to these parts of the rings than to those parts which lie more nearly trans to the strongly π-accepting carbonyl ligands. This is clearly seen in the alkylated ring, where the bond length variation is consistent with a degree of bond localization toward a diene structure. Such is not seen in the unsubstituted ring, where the esd's are greater and where the eclipsed orientation of the ring gives little preference in the use of $e_2{}^+$ and $e_2{}^-$ antibonding orbitals for back-donation. The adoption of a staggered conformation by the pentaalkylcyclopentadienyl ring may have a steric origin; the shortest intramolecular contact between the bromine and a cyclopentadienyl hydrogen atom in $Ru(C_5H_5)(CO)_2Br$ is 3.35 Å to H(4). This is acceptable for a bromine–hydrogen nonbonded distance; however, if the ethyltetramethylcyclopentadienyl compound were to adopt this conformation, the corresponding distance to a slightly out-of-plane methyl carbon atom would be 3.5 Å, which is rather short. The shortest such intramolecular contact in $Ru(C_5Me_4Et)(CO)_2Br$ is in fact 3.56 Å between the bromine and atom C(5).

We suggest that the conformation adopted by the five-membered rings and the bond length variations within the rings are related and note that they occur in other structures of this type. For example, in $[Fe(C_5H_5)(CO)_2]_2$[10a] and $[Ru(C_5Me_4Et)(CO)_2]_2$[11b] the symmetrically bonded five-membered rings are eclipsed with the terminal carbonyl ligand whereas in $[Fe(C_5Me_5)(CO)_2]_2$[10b] and $[Ru(C_5H_5)(CO)_2]_2$[11a] the rings adopt a diene type structure and are staggered with respect to the carbonyl groups.

As stated earlier, one of the objectives in undertaking this study was to see if the two crystal structures revealed features that could explain the differences in the chemistry and reactivity of $Ru(Cp')(CO)_2Br$, where Cp' = C_5H_5 or C_5Me_4Et. Undoubtedly C_5Me_4Et is a more electron-rich ligand than C_5H_5 and this can explain the formation of $Ru(Cp')(CO)Br_3$ (where Cp' = C_5Me_4Et but not C_5H_5); however, there is little, if any, evidence of this superior electron-donating ability in the two crystal structures.

---

(10) (a) R. F. Bryan and P. T. Greene, *J. Chem. Soc. A*, 3064 (1970); (b) R. G. Teller and J. M. Williams, *Inorg. Chem.*, **19**, 2770 (1980).

(11) (a) O. S. Mills and J. P. Nice, *J. Organomet. Chem.*, **9**, 339 (1969); (b) N. A. Bailey, S. L. Radford, J. A. Sanderson, K. Tabatabaian, C. White, and J. M. Worthington, *ibid.*, **154**, 343 (1978).

(12) (a) J. L. Atwood, R. Shakir, J. T. Malito, M. Herberhold, W. Kremnitz, W. P. E. Bernhagen, and H. G. Alt, *J. Organomet. Chem.*, **165**, 65 (1979); (b) J. T. Malito, R. Shakir, and J. L. Atwood, *J. Chem. Soc. Dalton Trans.*, 1253 (1980).

(13) (a) J. L. Atwood, R. D. Rogers, W. E. Hunter, C. Floriani, G. Fachinetti, and A. Chiesi-Villa, *Inorg. Chem.*, **19**, 3812 (1980); (b) D. J. Sikora, M. D. Rausch, R. D. Rogers, and J. L. Atwood, *J. Am. Chem. Soc.*, **103**, 1265 (1981).

(14) (a) I. W. Nowell, G. Fairhurst, and C. White, *Inorg. Chim. Acta*, **41**, 61 (1980); (b) T. C. McKenzie, R. D. Sanner, and J. E. Bercaw, *J. Organomet. Chem.*, **102**, 457 (1975); (c) R. D. Sanner, D. M. Duggan, T. C. McKenzie, R. E. Marsh, and J. E. Bercaw, *J. Am. Chem. Soc.*, **98**, 8351 (1976); (d) Yu. T. Struchkov, V. G. Andrianov, T. N. Sal'nikova, I. R. Lyatifov, and R. B. Materikova, *J. Organomet. Chem.*, **145**, 213 (1978); (e) L. R. Byers and L. F. Dahl, *Inorg. Chem.*, **19**, 277 (1980).

(15) J. A. Ibers, *J. Organomet. Chem.*, **73**, 389 (1974).

The crystal structures do confirm the previous suggestion[7] that the tendency of the C_5Me_4Et complex to undergo carbonyl substitution at a faster rate than the C_5H_5 complex arises from a stabilization of the transition state rather than from a ground-state effect; i.e., there is no evidence from the crystal structures that the carbonyl ligands in $Ru(C_5Me_4Et)(CO)_2Br$ are bonded any less strongly than in $Ru(C_5H_5)(CO)_2Br$. It is intriguing to speculate that the observed difference in reactivity results from the differences in the two structures. For instance, one could argue that in the case of the C_5Me_4Et complex, where there is evidence of a diene structure, dissociation of a carbonyl ligand is favored since this would reduce the steric constraints in the complex and so allow the C_5Me_4Et ligand to adopt a preferred η^5 coordination. The validity of such an argument must await further kinetic and structural studies on related compounds.

Acknowledgment. We thank the SERC for funds to purchase the diffractometer and Johnson Matthey for the generous loan of ruthenium trichloride.

Registry No. Ia, 32613-75-5; Ib, 72339-70-9.

Supplementary Material Available: Listings of hydrogen atom positional parameters, anisotropic thermal parameters, and observed structure amplitudes and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Tulane University, New Orleans, Louisiana 70118

Binuclear Cationic Complexes of Rhodium. 8. Crystal and Molecular Structure of the Dimetalated-Olefin Isocyanide Complex $[Rh_2(CNC(CH_3)_3)_4(\mu\text{-}F_3CC{=}CCF_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2](PF_6)_2\cdot 2(CH_3)_2CO$

JOEL T. MAGUE

Received July 17, 1982

The complex $[Rh_2(CNC(CH_3)_3)_4(\mu\text{-}F_3CC{=}CCF_3)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2](PF_6)_2\cdot 2(CH_3)_2CO$ crystallizes in the space group $C2/c$ with $a = 27.575$ (7) Å, $b = 11.432$ (5) Å, $c = 27.027$ (7) Å, $\beta = 103.07$ (2)°, $V = 8299$ (5) Å^3, and $Z = 4$. Diffraction data ($2\theta \leq 50.7$, Mo Kα) were collected on a Nicolet four-circle autodiffractometer, and the structure was solved by conventional methods. Discrepancy indices are $R_F = 0.045$ and $R_{wF} = 0.066$ for 6228 reflections with $I > 3\sigma(I)$. The dimeric dication has crystallographically imposed C_2 symmetry. The two rhodium atoms are bridged by two bis(diphenylphosphino)methane ligands and the fluorocarbon moiety, which is bound as a cis-dimetalated olefin. Neglecting the position of the second metal atom, the coordination about each metal approximates a square pyramid with one end of each phosphine ligand occupying trans basal sites. The other two basal sites are occupied by one end of the fluorocarbon moiety and one *tert*-butyl isocyanide ligand. The second isocyanide ligand occupies the apical site. The rhodium–rhodium distance of 2.9653 (6) Å is consistent with the presence of a single, albeit weak, metal–metal bond.

Introduction

Recently it was reported that electronegatively substituted acetylenes react with $[Rh_2(CNC(CH_3)_3)_4(DPM)_2](B(C_6H_5)_4)_2$ (DPM = bis(diphenylphosphino)methane) to form adducts having the composition $[Rh_2(CNC(CH_3)_3)_4(\text{acetylene})(DPM)_2](B(C_6H_5)_4)_2$.[1] From their ^{31}P NMR spectra it was evident that the acetylene had become bound in a symmetrical fashion and although the spectral parameters suggested binding as a cis-dimetalated olefin, the data were also consistent with its being bound with the central carbon–carbon axis perpendicular to the metal–metal vector. Also unexplained was the observation that although brownish orange solutions of the acetylene adduct became yellow on exposure to carbon monoxide, no evidence for coordinated carbon monoxide was found in the yellow product. The present study was undertaken to confirm the proposed mode of binding of the acetylene and to ascertain the course of the reaction with carbon monoxide. Since suitable crystals of the tetraphenylborate salts could not be obtained, we chose to study the hexafluorophosphate analogues. No difference in behavior between the two sets of salts was noted.

Experimental Section

Synthesis of $[Rh_2(CNC(CH_3)_3)_4(C_4F_6)(DPM)_2](PF_6)_2$. A solution of 0.40 g of $[Rh(CNC(CH_3)_3)_4(DPM)_2](PF_6)_2$[2] in 25 mL of dichloromethane was stirred under an atmosphere of hexafluorobut-2-yne in a septum-capped flask for 18 h, by which time the original purple color had changed to orange. The product was precipitated by addition of diethyl ether and recrystallized from dichloromethane/diethyl ether to give brownish microcrystals. Crystals of the acetone solvate suitable for the X-ray diffraction study were grown by the slow diffusion of diethyl ether into an acetone solution of the complex under nitrogen and obtained as dark orange-brown prisms (hereafter referred to as the brown crystals).

Reactions with Carbon Monoxide. A sample of the original recrystallized material prepared as described above was dissolved in acetone and the solution flushed with carbon monoxide whereupon it became bright yellow. Slow diffusion of diethyl ether into this solution under a carbon monoxide atmosphere yielded large yellow prisms (hereafter referred to as the yellow crystals).

As described below, X-ray diffraction studies on both the brown and yellow crystals showed that the only crystallographically detectable species present in each is $[Rh_2(CNC(CH_3)_3)_4(\mu\text{-}F_3CC{=}CCF_3)(DPM)_2](PF_6)_2$. Thus this acetylene adduct appears unaffected by treatment with carbon monoxide. We therefore suspected that the brown crystals contained an impurity which reacted with carbon monoxide to produce the observed color change. Thin-layer chromatography of a sample of the brown crystals showed this to be the case. Elution of samples of the brown and yellow compounds with tetrahydrofuran showed the former to consist of a minor, mobile brownish purple component and major immobile yellow component while the latter consisted only of the yellow, immobile component. The mobile component of the brown compound appeared to move at the same rate as purple $[Rh_2(CNC(CH_3)_3)_4(DPM)_2](PF_6)_2$ under the same conditions, and we tentatively ascribe the brown color of the brown crystals to the presence of a small amount of this complex, which cocrystallizes with the hexafluorobut-2-yne adduct. The color change on reaction of the brown crystals with carbon monoxide can then be attributed to the reaction of this impurity, which we have previously shown to form a yellow carbonyl adduct.[3] The absence

---

[1] Mague, J. T.; DeVries, S. H. *Inorg. Chem.* **1982**, *21*, 1632.
[2] Balch, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 8049.

0020-1669/83/1322-1158$01.50/0 © 1983 American Chemical Society