$[Cp_2Ti(OH)]$ should not be excluded.

As for the EPR parameters, a survey of Table I shows that the isotropic g values of the three halides examined show a uniform positive shift from Cl to I. A similar situation was found with the electroreduced zirconocene dihalides. In both cases no adequate information can be gathered from the anisotropic spectra of the bromides or the iodides because either of poor resolution or of the noncoaxial nature of the **A** and **g** tensors, so that all attempts to rationalize this phenomenon become purely speculative. Futhermore, similar information on d^1 metallocenes do not seem to be mentioned in literature, for example, in the case of the vanadocene dihalides. It is surprising, however, that this trend is exactly the opposite to that observed in the monomeric monohalides of the bis(pentamethylcyclopentadienyl)titanium compounds where the g values were reported to be 1.956, 1.953, and 1.939 for X = Cl, Br, and I, respectively.[28] It should be noted, however, that these measurements were made in pentane, and the bandwidths observed were over 60 G at room temperature. It is very unlikely that a difference in the ground state is responsible for this abnormally high negative shift compared to that for our compounds. Obviously a more detailed study in this area is needed.

Finally, the second and third reduction waves observed in the voltammogram of I call for some comments. Although a few speculations have been made about their significance, no conclusive evidence was provided in support. Our measurements on the ring-substituted analogues where Cp is replaced by Me-Cp or tetrahydroindenyl show not only that these two waves are always present but also that their reversibility is much more pronounced and is almost perfect in the latter substituted ring.[29] Strangely enough, both waves are absent in the voltammogram of $[\{Si(CH_3)_2(C_5H_4)_2\}TiCl_2]$[30] which exhibits only one reversible cathodic wave at −0.793 V against −0.800 V for I measured under the same conditions (ferrocene/ferrocenium couple as internal standard, $E^\circ = 0.51$ V vs SCE). It is surprising that bridging the rings in this case has such drastic effects on the electronic property of the metal so as to shift these two waves to much more negative potentials (below the solvent discharge) if they really exist. The reasons therefore should be sought elsewhere, and more studies are needed on this important feature in the chemistry of this family of compounds.

Acknowledgment. We are grateful to Mrs. Henique for technical assistance.

Registry No. I, 1271-19-8; Ie, 65466-17-3; II, 1293-73-8; IIe, 117469-83-7; III, 12152-92-0; IIIe, 117469-84-8; IV, 1271-18-7; V, 39333-86-3; VI, 39333-90-9; $[Cp_2Ti(MeOH)]^+$, 117469-85-9.

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(27) Corriu, R. J. P.; Dabosi, G.; Martineau, M. *J. Organomet. Chem.* **1981**, *222*, 195.

(28) Pattiasina, J. W.; Heeres, H. J., van Bolhuis, F.; Meetsema, A.; Teuben, J. H. *Organometallics* **1987**, *6*, 1004.

(29) Guery, D. Dissertation, University of Pierre and Marie Curie, Paris, 1982.

(30) Bajgur, C. S.; Tikkanen, W. R.; Petersen, J. L. *Inorg. Chem.* **1985**, *24*, 2539.

A Comparison of the Structures of *exo*- and *endo*-(η^5-Cyclopentadienyl)(η^3-2-methylallyl)ruthenium Carbonyl

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Received May 4, 1988

Crystal structure determinations of both the exo and endo isomers of $(C_5H_5)(C_4H_7)Ru(CO)$ reveal differences in interligand crowding which reflect the relative thermodynamic stability of the two conformers. In the less stable endo isomer, there are short hydrogen–hydrogen contacts between the C_5H_5 and C_4H_7 ligands, causing the Ru–C(Cp) distances to be unequal and the Ru–C distance to the central methylallyl carbon to lengthen [2.187 (7) Å] relative to the exo isomer [2.140(4) Å]. Another close contact between the allyl methyl and the CO ligand in the endo isomer forces nonlinearity [174.0 (8)°] in the Ru–C–O group. There is no significant intramolecular crowding in the exo isomer. The 2-methylallyl ligand is nonplanar in both structures, with the methyl carbon displaced 0.141 (9) Å from the allyl plane, toward the metal atom. *exo*-$(C_5H_5)(C_4H_7)RuCO$: monoclinic, space group $P2_1/c$, $a = 13.512$ (2) Å, $b = 6.004$ (1) Å, $c = 12.526$ (4) Å, $\beta = 108.42$ (2)°, $Z = 4$, $R = 0.028$ for 1734 reflections with $I > 3\sigma(I)$. *endo*-$(C_5H_5)(C_4H_7)RuCO$: orthorhombic, space group $Cmca$, $a = 8.814$ (1) Å, $b = 7.854$ (1) Å, $c = 27.659$ (4) Å, $Z = 8$, $R = 0.041$ for 1013 reflections with $I > 3\sigma(I)$.

Introduction

The capacity of some (η^5-cyclopentadienyl)(η^3-allyl)metal complexes to exist in endo and exo conformationally isomeric forms has been known for a number of years,[1] and the interconversions of some such isomers have been studied by dynamic NMR techniques.[2] Relative thermodynamic stabilities have been inferred from thermal isomerization data or observed concentration ratios for the

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(1) (a) Faller, J. W.; Incorvia, M. J. *Inorg. Chem.* **1968**, *7*, 840. (b) King, R. B.; Ishaq, M. *Inorg. Chim. Acta* **1970**, *4*, 258; (c) Faller, J. W.; Johnson, B. V.; Dryja, T. P. *J. Organomet. Chem.* **1974**, *65*, 395.

(2) See: Faller, J. W. *Adv. Organomet. Chem.* 1977, 16, *211*, for a review of this work.

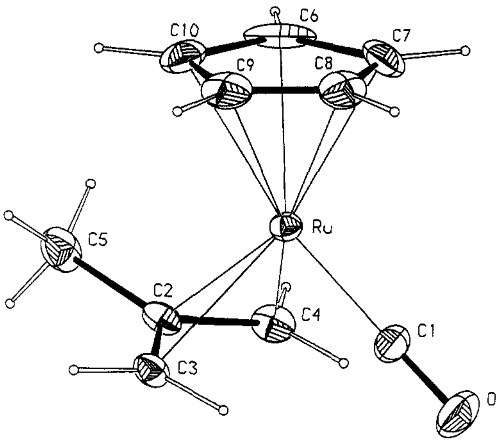

Figure 1. ORTEP plot of the exo conformer 1, with 25% probability thermal ellipsoids.

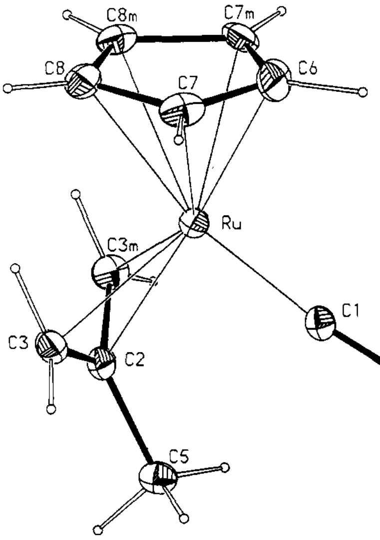

Figure 2. ORTEP plot of the endo conformer. An alternative site of 0.30 occupancy, with the cyclopentadienyl ring rotated 180°, is not shown. Thermal ellipsoids at 25% probability.

Table I. Crystal Data

	exo-Cp(C_4H_7)RuCO	endo-Cp(C_4H_7)RuCO
formula	$C_{10}H_{12}ORu$	$C_{10}H_{12}ORu$
fw	249.3	249.3
system	monoclinic	orthorhombic
space group	$P2_1/c$	*Cmca*
a, Å	13.512 (2)	8.814 (2)
b, Å	6.004 (1)	7.854 (1)
c, Å	12.526 (4)	27.659 (4)
β, deg	108.42 (2)	
V, Å^3	964.1 (4)	1914.7 (5)
Z	4	8
d_{calcd}, g cm^{-3}	1.717	1.729
μ(Mo Kα), cm^{-1}	15.45	15.56
max cryst dimens, mm	0.25 × 0.26 × 0.35	0.07 × 0.15 × 0.33
2θ range, deg	1–55	1–60
data collected	±*h*,*k*,*l*	*h*,*k*,*l*
total data	2707	1501
unique data ($I > 3\sigma(I)$)	1734	1013
R	0.028	0.041
R_w	0.039	0.055

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters[a]

atom	*x*	*y*	*z*	U_{eq} (Å^2)
		exo-(C_5H_5)(C_4H_7)Ru(CO)		
Ru	0.23009 (2)	0.08012 (5)	0.19402 (2)	0.0396 (1)
O	0.2302 (4)	−0.2188 (7)	0.0058 (3)	0.104 (3)
C(1)	0.2309 (4)	−0.1057 (8)	0.0774 (4)	0.061 (2)
C(2)	0.3906 (3)	0.0954 (7)	0.2951 (4)	0.051 (2)
C(3)	0.3590 (3)	−0.1291 (7)	0.2970 (4)	0.050 (2)
C(4)	0.3837 (3)	0.1893 (8)	0.1905 (4)	0.061 (2)
C(5)	0.4196 (4)	0.235 (1)	0.3988 (5)	0.071 (3)
C(6)	0.1548 (3)	0.3907 (8)	0.2283 (6)	0.100 (3)
C(7)	0.0899 (4)	0.290 (1)	0.1285 (5)	0.090 (3)
C(8)	0.0581 (3)	0.086 (1)	0.1556 (5)	0.076 (3)
C(9)	0.1033 (3)	0.060 (1)	0.2695 (5)	0.082 (3)
C(10)	0.1610 (3)	0.242 (1)	0.3147 (4)	0.082 (3)
		endo-(C_5H_5)(C_4H_7)Ru(CO)[b]		
Ru	0.000	0.14577 (7)	0.13304 (2)	0.0395 (2)
O	0.000	0.5223 (7)	0.1236 (3)	0.075 (4)
C(1)	0.000	0.3793 (9)	0.1245 (3)	0.046 (4)
C(2)	0.000	0.1328 (8)	0.0540 (3)	0.047 (3)
C(3)	0.1371 (6)	0.0665 (7)	0.0703 (2)	0.056 (3)
C(5)	0.000	0.288 (1)	0.0226 (3)	0.057 (4)
C(6)	0.000	0.141 (2)	0.2093 (5)	0.098 (9)
C(7)	0.1331 (9)	0.056 (1)	0.1964 (3)	0.063 (4)
C(8)	0.077 (1)	−0.096 (1)	0.1739 (3)	0.061 (4)
C(6′)	0.000	−0.075 (3)	0.1805 (9)	0.055 (11)
C(7′)	0.119 (2)	−0.003 (2)	0.1883 (6)	0.052 (9)
C(8′)	0.074 (2)	0.166 (2)	0.2118 (6)	0.061 (9)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$. [b] The atoms C(6′), C(7′), and C(8′) represent an alternative orientation of the cyclopentadienyl ring, with occupancy 0.30.

Table III. Bond Distances (Å) and Angles (deg) in *exo*- and *endo*-(C_5H_5)(C_4H_7)Ru(CO)

bond distances			bond angles	
	exo	endo		exo
Ru–C(1)	1.841 (4)	1.849 (7)	Ru–C(1)–O	179.2 (5)
Ru–C(2)	2.140 (4)	2.187 (7)	C(3)–C(2)–C(4)	117.9 (4)
Ru–C(3)	2.204 (4)	2.203 (5)	C(3)–C(2)–C(5)	121.2 (4)
Ru–C(4)	2.190 (4)		C(4)–C(2)–C(5)	120.6 (4)
Ru–C(6)	2.230 (4)	2.11 (3)	C(7)–C(6)–C(10)	106.4 (5)
Ru–C(7)	2.206 (4)	2.22 (2)	C(6)–C(7)–C(8)	108.5 (5)
Ru–C(8)	2.219 (4)	2.31 (1)	C(7)–C(8)–C(9)	106.7 (5)
Ru–C(9)	2.206 (4)		C(8)–C(9)–C(10)	110.5 (6)
Ru–C(10)	2.235 (4)		C(9)–C(10)–C(6)	107.9 (5)
O–C(1)	1.123 (5)	1.123 (8)		
C(2)–C(3)	1.416 (5)	1.390 (6)		endo
C(2)–C(4)	1.402 (6)		Ru–C(1)–O	174.0 (8)
C(2)–C(5)	1.490 (7)	1.50 (1)	C(3)–C(2)–C(3m)	120.6 (7)
C(6)–C(7)	1.421 (10)	1.40 (3)	C(3)–C(2)–C(5)	119.5 (4)
C(7)–C(8)	1.364 (9)	1.43 (1)	C(7)–C(6)–C(7m)	114 (3)
C(8)–C(8m)		1.36 (3)	C(6)–C(7)–C(8)	103 (2)
C(8)–C(9)	1.372 (8)		C(7)–C(8)–C(8m)	110 (1)
C(9)–C(10)	1.358 (9)			
C(6)–C(10)	1.383 (9)			

two isomers in cyclopentadienyl allyl complexes of Mo, W, and Fe.[1,3] As the major solution isomer is usually the only one to crystallize from mixtures of the two, it has not heretofore been possible to make a direct comparison of the crystallographic structures of the endo and exo isomers of the same complex. The characterizations of *exo*- and *endo*-(η^5-cyclopentadienyl)(η^3-2-methylallyl)ruthenium carbonyl (1 and 2, respectively, see Figures 1 and 2) were described by us (D.H.G. and W.-L.H.) several years ago;[4] these isomers do not interconvert in solution at room temperature; thus it has been possible to obtain X-ray quality crystals of both compounds. It was shown that thermal endo → exo isomerization takes palce at 130–140 °C, leading to endo/exo ratios less than 0.02 and establishing the exo isomer as the more stable one. We report herein the crystal structures of these two isomers and

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(3) Fish, R. W.; Giering, W. P.; Marten, D.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *105*, 101.

(4) Gibson, D. H.; Hsu, W.-L.; Steinmetz, A. L.; Johnson, B. V. *J. Organomet. Chem.* **1981**, *208*, 89.

consider their relative stability in terms of their molecular structures.

Results and Discussion

Crystal data are shown in Table I, fractional coordinates are listed in Table II, and bond distances and angles are given in Table III. The structure and atom numbering are shown in Figure 1 for **1** and in Figure 2 for **2**.

The endo complex **2** lies on a crystallographic mirror plane. Thus, the ruthenium atom, the carbonyl, C(2) and C(5) of the 2-methylallyl ligand, and C(6) of the cyclopentadienyl are coplanar. In the exo complex **1** this mirror symmetry is approximately present, the main departure being a slight rotation of the cyclopentadienyl ring.

The cyclopentadienyl ring is planar in both complexes, and the distance, 1.883 (4) Å, of Ru from the Cp plane is the same. The individual distances of Ru to the Cp carbons in **1** are equal within experimental error. However, in **2** these distances are significantly unequal, the Ru–C(6) distance, 2.11 (3) Å, being shortest and the two Ru–C(8) distances, 2.31 (1) Å, longest. This slippage in the cyclopentadienyl ring in the endo complex appears to be a consequence of repulsive contacts between the Cp carbons C(8) and C(8m) and the methylallyl ligand, especially the hydrogen atoms on C(3) and C(3m) (Figure 2). Assuming the hydrogen atoms on C(3), and C(3m), to be in the plane of the allyl, their distance to the Cp hydrogens on C(8), and C(8m), would be 2.23 Å. This contact, which is less than the accepted[5] 2.4-Å van der Waals distance, is undoubtedly relieved by out-of plane bending of the allyl hydrogens, as is the case in a related molybdenum compound.[6] Another manifestation of these repulsive interactions is that the Ru–C(2) distance of 2.187 (7) Å is longer than the corresponding distance, 2.140 (4) Å, in the exo complex, indicating a displacement of the methylallyl ligand away from the cyclopentadienyl in **2**. This causes the three Ru–C(allyl) distances in **2** to be essentially equal. By contrast, in **1** the central allyl carbon is significantly closer to the ruthenium atom than the two terminal carbon atoms.

While in the exo complex the Ru–C(1)–O geometry is linear within experimental error, there is a 6-deg bend in the endo complex. This distortion is attributed to repulsion between the allylmethyl group and the carbonyl oxygen, the C(5)···O distance being 3.35 (1) Å, slightly less than the 3.40-Å sum of the accepted van der Waals radii.[5]

This structural comparison shows that in the endo conformation the 2-methylallyl ligand experiences repulsive contacts with both the Cp and the carbonyl ligands, while in the exo conformation both interferences are relieved. This observation is a plausible explanation for the greater stability of the exo isomer.

It is of interest to compare the structures of **1** and **2** to two related molybdenum compounds. The complex *endo*-(η^5-cyclopentadienyl)(η^3-2-methylallyl)molybdenum dicarbonyl[6] shows a slippage of the cyclopentadienyl ring, which manifests itself in longer Mo–C distances to those Cp carbons nearest the methylallyl ligand, the range of Mo–C(Cp) distances being 0.071 (4) Å. Also, the three Mo–C(allyl) distances are equal within experimental error. It is reasonable to assume that these effects, which are found in both the endo molybdenum complex and in **2**, arise from the repulsive allyl–Cp interaction.

The complex bis(η^3-allyl)(η^5-cyclopentadienyl)molybdenum,[7] with two allyl ligands in endo conformation, likewise has Mo–C(allyl) distances which are very nearly equal.

In the *exo*-(η^5-cyclopentadienyl)(η^3-allyl)molybdenum dicarbonyl[8] the Mo–C(Cp) distances are more nearly equal, the difference between the longest and shortest being a marginally significant 0.027 (7) Å. Also, the central carbon of the allyl ligand is closer to the metal atom than the terminal carbons; this is usually found to be the case in allyl complexes in the exo conformation.[8–10]

Both isomers show bending of the 2-methyl group of the methylallyl ligand toward the metal atom. The displacement of the methyl carbon from the allyl plane is 0.141 (9) Å in both **1** and **2**, comparable to the value 0.111 (3) Å reported for the molybdenum 2-methylallyl complex.[6] The allyl carbon–carbon bond lengths in the endo complex are equal by symmetry; in the exo complex they are also equal, within experimental error. This is in contrast to the asymmetrically substituted complexes studied by Faller[8] and Legzdins[11] in which distortion to σ–π complexes occurs.

The dihedral angle between the cyclopentadienyl and the allyl (C2,C3,C4) planes in **1** is 16.5°. In **2** the corresponding dihedral angle is 68.5°, compared to 73.5° in the endo molybdenum complex.[6]

Experimental Section

Crystal Structure Determinations. Pale yellow crystals suitable for X-ray work were obtained by slow crystallization from *n*-pentane at −15 °C. In each case the crystal was mounted in a capillary for X-ray examination and data collection. All data were collected at room temperature on a Syntex $P2_1$ diffractometer with graphite-monochromated Mo Kα radiation; λ(Mo Kα) = 0.71069 Å. Unit cell parameters (Table I) and standard deviations were obtained by least-squares fit to 15 reflections, well distributed in reciprocal space and lying in the 2θ range 20–25°. Intensity data were collected in the $2\theta{:}\theta$ scan mode, with scans from 0.8 deg below Kα_1 to 0.8 deg above Kα_2 and a variable scan speed of 2.5–12.0 deg/min. Background counts stationary, with total background time/scan time of 0.8. Other data collection parameters are given in Table I. Three standard reflections were monitored and showed no significant decay. The data were corrected for Lorentz and polarization effects, but not for absorption.

The space group $P2_1/c$ of **1** is uniquely determined by the observed systematic absences. The position of the Ru atom was determined from the Patterson function, and the positions of the oxygen and carbon atoms were determined from an electron density Fourier synthesis phased on the Ru atom. The hydrogen atoms of the Cp and 2-methylallyl ligands were placed at calculated positions [C–H = 0.95 Å, $B(H) = B(C) + 1.0$] during refinements. Full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$ was carried out by using anisotropic thermal parameters of all non-hydrogen atoms and with the positional and thermal parameters of all hydrogen atoms fixed. The weights were taken as $w = [\sigma^2(I) + (kF_o^2)^2]^{-1/2}$ where $k = 0.05$ was chosen to make $w\Delta F^2$ uniformly distributed in $|F_o|$. An extinction correction of the type[12] $F = F_o(1 + gI_c)$ was applied in the final cycles, and the parameter g refined to 0.36×10^{-6}. The final value of R was 0.028, R_w = 0.039.

The X-ray data for **2** showed systematic absences which were consistent with both the centrosymmetric space group *Cmca* (D_{2h}^{18},

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[5] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press; Ithaca, NY, 1960; p 260.

[6] Murrall, N. W.; Welch, A. J. *Acta Crystallogr.* **1984** *C40*, 401.

[7] Jolly, J. W.; Krüger, C.; Romao, C. C.; Romao, M. J. *Organometallics* **1984** *3*, 936.

[8] Faller, J. W.; Chodosh, D. F.; Katahira, D. *Organometallics* **1980** *187*, 227.

[9] Allen, S. R.; Baker, P. K.; Barnes, S. G.; Bottrill, M.; Green, M.; Orpen, G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1983**, 927.

[10] Batsanov, A. S.; Struchkov, Yu. T. *J. Organomet. Chem.* **1984**, *265*, 305.

[11] Greenhough, T. J.; Legzdins, P.; Martin, D. T.; Trotter, J. *Inorg. Chem.* **1979**, *18*, 3268.

[12] Stout, G. H.; Jensen, L. H. *X-Ray Structure Determination*; Macmillan: New York, 1968; p 412.

No. 64) and the noncentrosymmetric space group $C2cb$ (standard setting $Aba2$, C_{2v}^{17}, No. 41). With $Z = 8$ (Table I) the space group $Cmca$ demands that the formula unit possesses a mirror plane and that the Ru, O, C(1), C(4), C(5), C(6) atoms lie at $x = 0$ and $^1/_2$. In $C2cb$ no symmetry demands are placed on the formula unit. $Cmca$ was initially assumed, and this space group was subsequently verified by the unambiguous, refined structure. Interpretation of the three-dimensional Patterson function gave the Ru coordinates. The carbon and oxygen atoms were found from a Fourier synthesis phased on Ru. Following several cycles of anisotropic least-squares refinement, the thermal ellipsoid of the cyclopentadienyl carbon lying on the mirror plane, C(6), was found to be abnormally extended in the direction perpendicular to the mirror plane. This was taken to indicate some disorder in the cyclopentadienyl ring, with a fraction of the cyclopentadienyls occupying a position rotated by 180° about the ring axis. By trial, the occupany of this rotated position was found to be 0.3. Refinement of the major component, with occupany 0.7, gave well-behaved thermal ellipsoids and improved bond distances. The hydrogen atoms of the Cp and 2-methylallyl ligands were then placed at calculated positions [C–H = 0.95 Å, $B(\mathrm{H}) = B(\mathrm{C}) + 1.0$] during refinement, with the positional and thermal parameters fixed. Full-matrix refinement with weights $w = [\sigma^2(I) + (kF_o{}^2)^2]^{1/2}$ and $k = 0.08$ gave a final R value of 0.041, $R_w = 0.055$, for 1013 observed reflections. An extinction correction was included in the structure factor calculation and was refined during final least-squares refinement, giving $g = 4.87 \times 10^{-6}$.

Both structure factor calculations used atomic scattering factors for C, O, and Ru, with anomalous dispersion from Cromer and Liberman,[13] and for bonded H from Stewart, Davidson and Simpson.[14]

Registry No. 1, 78037-33-9; 2, 77933-78-9.

Supplementary Material Available: Listings of anisotropic temperature factors, calculated hydrogen atom parameters, and data on least-squares planes (3 pages); listings of observed and calculated structure factor amplitudes (19 pages). Order information is given on any current masthead page.

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(13) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(14) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Versatile Behavior of Hydrido Monometallic or Heterobimetallic Carbonyl Anions toward Dichlorophosphines and 1,1-Dichlorodiphosphines

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Received March 14, 1988

The reactivity of 1,1-dichlorodiphosphine $(i\text{-}\mathrm{Pr_2N})_2\mathrm{P{-}PCl_2}$ (**5**) toward $[\mathrm{NEt_4}][\mathrm{HW(CO)_5}]$ (**2**) and $[\mathrm{NEt_4}][\mathrm{HFe(CO)_4}]$ (**1b**) has been investigated. The first reaction leads to the neutral difunctionalized diphosphine complex $(i\text{-}\mathrm{Pr_2N})\mathrm{P(Cl){-}P(H)}(\mathrm{N}\text{-}i\text{-}\mathrm{Pr_2})\mathrm{W(CO)_5}$ (**9**), implying diisopropylamino group migration, while the second reaction affords $[\mathrm{NEt_4}][(i\text{-}\mathrm{Pr_2N})\mathrm{P(H)[Fe(CO)_4]{-}P(H)[Fe(CO)_4]_2}]$ (**10**) in which a phosphorus–nitrogen bond has been cleaved. The structures of **9** and **10** have been determined by X-ray diffraction. **9** is triclinic, space group $P1$, with $a = 9.887$ (4) Å, $b = 10.349$ (4) Å, $c = 14.309$ (4) Å, $\alpha = 75.92$ (3)°, $\beta = 75.50$ (3)°, $\gamma = 64.72°$, and $Z = 2$. The structure has been solved and refined to R and R_w values of 0.028 and 0.027, respectively, by using 3898 reflections. **10** is monoclinic, space group $P2_1/n$, with $a = 10.018$ (5) Å, $b = 29.892$ (13) Å, $c = 12.337$ (5) Å, $\beta = 100.66$ (4)°, and $Z = 4$. The structure has been refined to R and R_w values of 0.086 and 0.081, respectively, by using 2644 reflections. The reaction of dichlorophosphines $\mathrm{RPCl_2}$ with $[\mathrm{PPh_4}][\mathrm{HFeW(CO)_9}]$ (**3**) has also been examined: the $[\mathrm{PPh_4}][(\mu\text{-}\mathrm{RP(Cl)})[\mathrm{Fe(CO)_4}][\mathrm{W(CO)_5}]]$ complexes have been obtained (R = Ph, **14a**; R = Me, **14b**; R = 2,5-dimethyl-1,2,3-σ^2-diazaphosphole, **14c**). The formation of $[\mathrm{PPh_4}][\mathrm{PhP(H)[Fe(CO)_4][W(CO)_5]}]$ (**15a**) from $\mathrm{PhPCl_2W(CO)_5}$ and $[\mathrm{PPh_4}][\mathrm{HFe(CO)_4}]$ (**1a**), which requires 2 equiv of the iron anion, points out the specificity of the reaction of **3**.

Introduction

Over the last 5 years, a significant volume of research has been devoted to the study of the reactivity of $\mathrm{Na_2Fe(CO)_4}$ or $\mathrm{Na_2M_2(CO)_{10}}$ dianions (M = Cr, Mo, or W) toward dichlorophosphines, $\mathrm{RPCl_2}$. Depending on the nature of the organometallic fragments, various compounds of the type $[(\mathrm{CO})_n\mathrm{M}]_2\mathrm{PR}$, $[((\mathrm{CO})_n\mathrm{M})_2(\mathrm{PR})_2\mathrm{M(CO)}_n]$, and related species have been prepared.[1] In contrast, very few

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