trum is consistent with ^{65}Cu,^{63}Cu hyperfine coupling of 3.5 G. In a similar fashion, 4 undergoes chemical reduction to give the species $[(Cp_2Ti(\mu\text{-}SCH_2CH_2CH_2S)_2TiCp_2)Ag]^0$ (6). The EPR signal for 6 is centered at $g = 1.9817$. In addition, hyperfine couplings to ^{107}Ag,^{109}Ag and ^{47}Ti,^{49}Ti of 5.0 and 11.0 G respectively are observed. These g values and Ti hyperfine parameters are typical of Ti-based radicals. The hyperfine coupling to the encapsulated metal ions in 5 and 6 compare with the ^{65}Cu,^{63}Cu hyperfine couplings of 9.5 G seen in $[Cp_2V(\mu\text{-}SEt)_2CuPR_3]^+$ and the ^{103}Rh hyperfine coupling of 2.8 G seen in $[Cp_2Ti(\mu\text{-}SCH_2CH_2CH_2PPh_2)_2Rh]^0$.[13,15] Solutions of the reduced species 5 and 6 are unstable, and thus, isolation of the reduced compounds was not achieved. A minor additional EPR signal is also observed at $g = 1.9791$ and $g = 1.9794$ in the EPR spectra of 5 and 6, respectively. These signals could be reproduced via reduction of the free metalloligands 1 and 2, and thus, these signals are attributed to the demetalated degradation products of 5 and 6. Similar instability has been observed for related reduced ELHB complexes.[13,15] Further reduction to what is potentially a Ti(III)/M(I)/Ti(III) species proceeds with complex degradation, as evidenced by the irreversible reduction waves observed at −1.56 and −1.53 V vs Ag/AgCl for 3 and 4, respectively. As well, an irreversible oxidation wave, presumably attributable to Cu(I)/Cu(II) oxidation, is observed at 1.13 V for 3. Although Cu(II) complexes of organic S_4 macrocycles have been described by several authors,[38] for reasons that are not clear a square-planar environment about Cu(II) presented by the macrocycle 3 is not stable. However, studies in which the titanocene macrocycle 2 and its zirconocene analogue accommodate the square-planar coordination spheres for Rh(I) and Ir(I) are ongoing.

Summary. The present results offer synthetic routes to a new class of redox-active, macrocyclic ligands. Further, the data confirm that these early-metal macrocycles act as effective metalloligands for the encapsulation of late metals. The electrochemical and EPR data indicate that such early-metal macrocycles are capable of acting as electron reservoirs, and thus, work is continuing both to stabilize the reduced complexes and to examine the participation of the early metal in reactions centered on the late metal.

Acknowledgment. Financial support from the NSERC of Canada is gratefully acknowledged. The donors of the Petroleum Research Fund, administered by the American Chemical Society, are also thanked for financial support. The University of Windsor is thanked for the award of a Research Professorship.

Registry No. 1, 137232-40-7; 2, 137232-41-8; 3, 137232-43-0; 4, 137232-45-2; $4\cdot H_2O\cdot 0.75CH_2Cl_2$, 137255-49-3; 5, 137232-46-3; 6, 137232-47-4; $(SCH_2CH_2CH_2S)_2$, 6573-59-7; $NCSCH_2CH_2CH_2SCN$, 7314-74-1; Cp_2TiCl_2, 1271-19-8; $Cp_2Ti(PMe_3)_2$, 95936-00-8; Cp_2TiPh_2, 1273-09-2; $[Cu(NCMe)_4]BF_4$, 15418-29-8; $AgBPh_4$, 14637-35-5; Cp_2Co, 1277-43-6; ethanedithiol, 540-63-6; propanedithiol, 109-80-8.

Supplementary Material Available: Tables of thermal and hydrogen atom parameters (11 pages); a table of $10F_o$ and $10F_c$ values (27 pages). Ordering information is given on any current masthead page.

---

(38) A recent reference in this area is: Desper, J. M.; Gellman, S. H. *J. Am. Chem. Soc.* 1991, *113*, 704.

Synthesis and Structure of Two Organozirconocenes with α Nitrogen Substituents

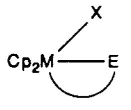
Timothy V. Lubben, Karl Plössl, Jack R. Norton,* Mary M. Miller, and Oren P. Anderson

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

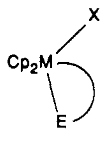
Received May 24, 1991

Two zirconocene derivatives with organic ligands containing α nitrogen substituents have been prepared, and their structures have been determined by single-crystal X-ray diffractometry. The reaction of $Cp_2Zr(Me)(\eta^2\text{-}CHPhNMe_2)$ with CF_3CO_2H yields $Cp_2Zr(O_2CCF_3)(\eta^2\text{-}CHPhNMe_2)$ (8). The reaction of $Cp_2Zr(CMeN^tBu)(O_2CCF_3)$ with $Cp_2Zr(Me)H$ yields $Cp_2Zr(\eta^2\text{-}CMeN^tBu)(\mu\text{-}O,O'\text{-}O_2CHCF_3)Zr(Me)Cp_2$ (9). The structure of 8 was determined at −125 °C; it crystallizes in space group $P2_1/n$, with $a = 8.839$ (2) Å, $b = 16.491$ (4) Å, $c = 13.887$ (5) Å, $\beta = 103.22$ (2)°, and $Z = 4$. The structure of 9 was determined at −130 °C; it crystallizes in space group $P2_1/n$, with $a = 12.085$ (2) Å, $b = 14.922$ (3) Å, $c = 15.927$ (2) Å, $\beta = 91.50$ (1)°, and $Z = 4$. In both 8 and 9 the nitrogen is coordinated inside the carbon and oxygen ligand atoms.

It is difficult to determine spectroscopically whether a donor atom E attached to an organic ligand R in a metallocene complex $Cp_2M(R)X$ is bound "inside" (A) or "outside" (B).[1]



inside
A



outside
B

Zirconocene chemistry offers examples of both structural types. For example, acyl ligands, with E being oxygen, have their oxygen atoms coordinated outside when they are generated by the carbonylation of organozirconocenes but eventually rearrange so that their oxygen atoms are coordinated inside.[2] When E is nitrogen, X-ray crystallography has usually shown the nitrogen atom to be coordinated inside, for example in the aldimine ligand in 1[3] and in the iminoacyl ligand in 2.[4]

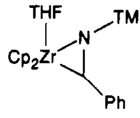
---

(1) The "inside" and "outside" terminology is due to: Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* 1985, *107*, 4440.

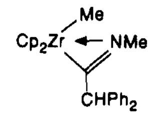
(2) Erker, G.; Rosenfeldt, F. *Angew. Chem., Int. Ed. Engl.* 1978, *17*, 605; *J. Organomet. Chem.* 1980, *188*, C1–C4.

(3) Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* 1989, *111*, 4486.

0276-7333/92/2311-0122$03.00/0

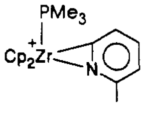


1

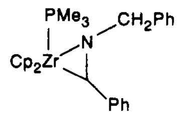


2

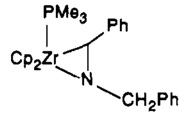
However, there is at least one case in which such a nitrogen atom prefers to be coordinated outside: X-ray crystallography has established the structure shown for the more stable isomer of the η^2-picolyl cation **3**.[5] In other cases the inside and outside structures are about equal in energy: ^{1}H NMR spectroscopy has shown a mixture of both isomers in solution for two analogues of **1** (**4**[3] and **5**[6,7]) and for **6**, the predecessor of **3**.[5]



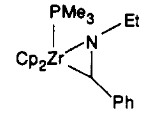
3



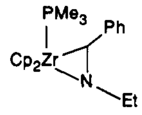
4A



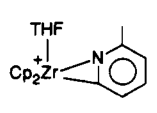
4B



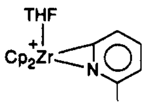
5A



5B

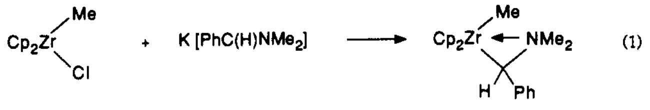


6A



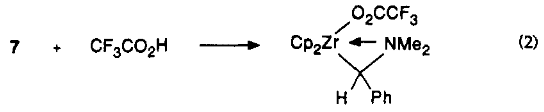
6B

We therefore attempted to determine the structure of **7**, one of a series of aminoalkyl zirconocene complexes we had recently prepared from zirconocene halides and appropriate organometallic reagents (eq 1).[8] However, **7** failed to give crystals suitable for X-ray analysis. We therefore removed the methyl ligand of **7** with CF_3CO_2H and obtained the analogous trifluoroacetate complex **8** (eq 2). We now report an X-ray structure determination of **8** (bis(η^5-cyclopentadienyl)((dimethylamino)benzyl)(trifluoroacetato)zirconium(IV)).



(1)

7



(2)

8

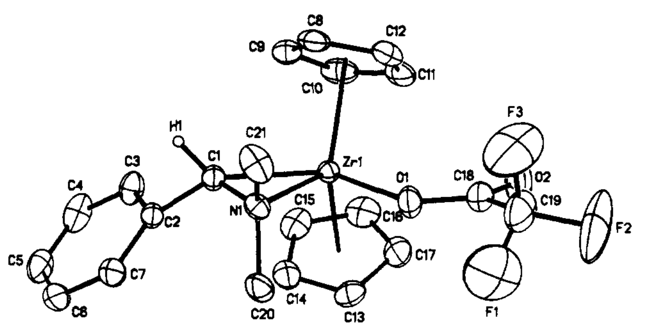


Figure 1. Structure of compound **8**. Hydrogen atoms (except H1) are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

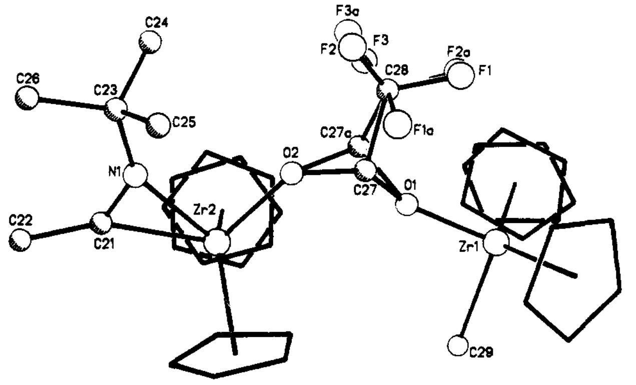
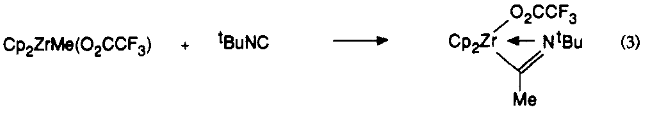


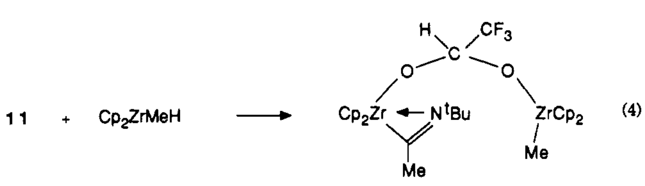
Figure 2. Structure of compound **9**.

We also report the structure of **9**, an iminoacyl complex with an alkoxide ligand. This compound was obtained when the attempted reduction of the iminoacyl ligand[9] in **11** (prepared from **10**[10] and ^{t}BuNC, eq 3) with $Cp_2Zr(Me)H$ resulted (eq 4) in reduction of the trifluoroacetate ligand instead (a reaction analogous to the reduction of an acetate ligand reported by Cutler and co-workers[11]). This X-ray structure determination has not only allowed us to determine whether the nitrogen of **9** is inside or outside but



(3)

10 **11**



(4)

9

---

[4] Bristow, G. S.; Lappert, M. F.; Atwood, J. L.; Hunter, W. E. Unpublished work (cited in: Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Halsted: New York, 1986; p 223).

[5] Jordan, R. F.; Taylor, D. F.; Baenziger, N. C. *Organometallics* **1990**, *9*, 1546.

[6] Filley, J.; Lubben, T. V.; Plössl, K.; Norton, J. R. Unpublished work. The ratio of **5A** to **5B** is constant at 2.3:1 whether they are prepared from $Cp_2Zr(Me)N(Et)CH_2Ph$ (the method of ref 3) or from "Cp_2Zr"[7] and PhCH=NEt, so the ratio is thermodynamic rather than kinetic.

[7] Negishi, E.; Cederbaum, F. W.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829.

[8] Plössl, K.; Norton, J. R.; Davidson, J. G.; Barefield, E. K. *Organometallics*, in press.

[9] For other reductions of this type see: (a) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. (b) Frömberg, W.; Erker, G. *J. Organomet. Chem.* **1985**, *280*, 355.

[10] Martin, B. D.; Matchett, S. A.; Norton, J. R.; Anderson, O. P. *J. Am. Chem. Soc.* **1985**, *107*, 7952.

[11] Cutler, A.; Raja, M.; Todaro, A. *Inorg. Chem.* **1987**, *26*, 2877.

Table I. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)^a for 8

atom	*x*	*y*	*z*	$U_{iso}{}^b$
Zr1	1419 (1)	6812 (1)	6617 (1)	19 (1)
O1	2345 (3)	6355 (2)	5375 (2)	30 (1)
O2	854 (5)	6855 (2)	3958 (2)	61 (1)
N1	3587 (4)	6068 (2)	7363 (2)	22 (1)
F1	3714 (5)	5457 (3)	4206 (3)	88 (2)
F2	2712 (5)	6119 (3)	2967 (2)	104 (2)
F3	4440 (5)	6662 (3)	4106 (3)	97 (2)
C1	2966 (4)	6459 (2)	8124 (3)	22 (1)
C2	2581 (4)	6039 (2)	8997 (3)	23 (1)
C3	1678 (5)	6480 (3)	9527 (3)	32 (1)
C4	1343 (5)	6182 (3)	10381 (3)	40 (2)
C5	1860 (6)	5432 (3)	10731 (3)	43 (2)
C6	2734 (6)	4987 (3)	10220 (3)	43 (2)
C7	3085 (5)	5285 (3)	9369 (3)	33 (1)
C8	3101 (5)	8098 (2)	6934 (3)	33 (1)
C9	1880 (6)	8198 (2)	7421 (3)	37 (1)
C10	486 (5)	8233 (3)	6710 (4)	39 (2)
C11	826 (5)	8141 (3)	5776 (3)	38 (1)
C12	2439 (5)	8075 (2)	5920 (3)	33 (1)
C13	−224 (5)	5548 (3)	6193 (3)	36 (1)
C14	−237 (5)	5731 (3)	7171 (3)	37 (1)
C15	−1004 (5)	6467 (3)	7193 (3)	38 (2)
C16	−1511 (5)	6732 (3)	6210 (4)	42 (2)
C17	−1013 (5)	6177 (3)	5591 (3)	40 (2)
C18	1988 (6)	6497 (3)	4452 (3)	36 (1)
C19	3226 (6)	6185 (4)	3928 (3)	47 (2)
C20	3453 (5)	5176 (2)	7196 (3)	29 (1)
C21	5171 (5)	6315 (3)	7296 (3)	36 (1)

^{a} Estimated standard deviations in the least significant digits are given in parentheses. ^{b} The equivalent isotropic *U* is defined as one-third of the trace of the $\mathbf{U}_{ij}$ tensor.

Table II. Selected Bond Distances (Å)^a and Angles (deg)^a for 8

Zr1–C1	2.297 (3)	C18–O1	1.269 (5)
Zr1–N1	2.312 (3)	C18–O2	1.229 (6)
Zr1–O1	2.205 (3)		
C1–N1	1.448 (5)	Zr1–Cp1^b	2.228
N1–C20	1.482 (5)	Zr1–Cp2	2.228
N1–C21	1.489 (5)		
C1–Zr1–N1	36.6 (1)	C1–N1–Zr1	71.1 (2)
N1–Zr1–O1	75.6 (1)	C20–N1–C21	107.7 (3)
C1–Zr1–O1	112.1 (1)		
Zr1–C1–N1	72.2 (2)	Zr–O1–C18	132.5 (3)
		Cp1–Zr1–Cp2	127.9

^{a} Estimated standard deviations in the least significant digits are given in parentheses. ^{b} Cp*X* is the centroid of a C_5H_5 ligand.

Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)^a for 9

atom	*x*	*y*	*z*	$U_{iso}{}^b$
F1	3196 (5)	7264 (4)	4467 (4)	39 (2)
F2	4730 (5)	7920 (4)	4307 (4)	42 (1)
F3	3683 (5)	8452 (4)	5284 (4)	47 (1)
F1a	4702 (7)	6817 (6)	4466 (5)	51 (2)
F2a	2994 (7)	7465 (6)	4652 (6)	31 (2)
F3a	4483 (7)	8256 (6)	4459 (5)	37 (2)
Zr1	2491 (1)	6011 (1)	6372 (1)	21 (1)*
Zr2	6337 (1)	7613 (1)	7069 (1)	18 (1)*
O1	3777 (3)	6762 (2)	6111 (2)	24 (1)*
O2	5419 (3)	7546 (2)	5934 (2)	27 (1)*
N1	7515 (3)	8340 (3)	6270 (2)	24 (1)*
C1	1553 (7)	7545 (5)	6459 (9)	29 (2)
C1a	1317 (18)	7414 (15)	6066 (15)	33 (4)
C2	845 (9)	6972 (8)	5995 (6)	37 (2)
C2a	606 (17)	6686 (16)	6085 (13)	30 (5)
C3	431 (6)	6308 (5)	6549 (7)	28 (2)
C3a	566 (17)	6302 (14)	6891 (17)	34 (5)
C4	944 (6)	6460 (5)	7357 (5)	27 (1)
C4a	1315 (20)	6941 (18)	7415 (13)	38 (5)
C5	1642 (7)	7229 (7)	7291 (6)	31 (2)
C5a	1625 (15)	7520 (13)	6831 (19)	29 (5)
C6	2888 (5)	5247 (4)	5004 (4)	48 (2)*
C7	1724 (5)	5141 (4)	5127 (3)	36 (2)*
C8	1613 (5)	4564 (4)	5837 (3)	36 (2)*
C9	2684 (6)	4328 (4)	6141 (4)	51 (2)*
C10	3473 (5)	4745 (4)	5625 (5)	56 (2)*
C11	6176 (6)	8974 (5)	8027 (5)	24 (2)
C11a	6140 (12)	8553 (11)	8397 (8)	18 (3)
C12	5780 (8)	8223 (6)	8468 (4)	21 (2)
C12a	5227 (14)	7942 (9)	8367 (9)	20 (3)
C13	4767 (8)	7938 (6)	8044 (7)	27 (2)
C13a	4531 (10)	8160 (10)	7690 (10)	15 (2)
C14	4574 (7)	8506 (6)	7365 (5)	30 (2)
C14a	4960 (11)	8906 (8)	7293 (7)	16 (2)
C15	5449 (8)	9147 (6)	7321 (5)	33 (2)
C15a	5980 (10)	9164 (8)	7727 (8)	18 (2)
C16	7387 (4)	6192 (3)	6715 (4)	32 (2)*
C17	7779 (4)	6450 (3)	7524 (3)	31 (2)*
C18	6897 (5)	6376 (3)	8079 (3)	32 (2)*
C19	5965 (4)	6056 (3)	7625 (4)	32 (2)*
C20	6266 (4)	5942 (3)	6794 (4)	33 (2)*
C21	7947 (4)	8299 (3)	6995 (3)	24 (1)*
C22	9057 (4)	8621 (4)	7364 (4)	33 (2)*
C23	7810 (4)	8705 (4)	5436 (3)	31 (2)*
C24	6900 (5)	9382 (4)	5196 (4)	44 (2)*
C25	7776 (5)	7894 (4)	4840 (3)	42 (2)*
C26	8952 (5)	9150 (4)	5434 (4)	47 (2)*
C27	4589 (6)	7064 (5)	5563 (5)	21 (2)
C27a	4259 (11)	7547 (9)	5755 (8)	33 (3)
C28	4061 (5)	7621 (5)	4888 (4)	53 (2)*
C29	3060 (4)	5434 (4)	7648 (3)	37 (2)*

^{a} Estimated standard deviations in the least significant digits are given in parentheses. ^{b} For values with asterisks, the equivalent isotropic *U* is defined as one-third of the trace of the $\mathbf{U}_{ij}$ tensor.

Table IV. Selected Bond Distances (Å)^a and Angles (deg)^a for 9

Zr2–C21	2.206 (5)		
Zr2–N1	2.216 (4)	Zr1–Cp1^b	2.247
Zr2–O2	2.099 (3)	Zr1–Cp2	2.227
C21–N1	1.255 (6)	Zr2–Cp3	2.238
N1–C23	1.487 (7)	Zr2–Cp4	2.237
Zr1–O1	1.968 (3)		
C21–Zr2–O2	115.0 (2)		
C21–Zr2–N1	33.0 (2)	Cp1–Zr1–Cp2	129.4
N1–Zr2–O2	82.0 (1)	Cp3–Zr2–Cp4	129.3
Zr2–C21–N1	74.0 (3)		

^{a} Estimated standard deviations in the least significant digits are given in parentheses. ^{b} Cp*X* is the centroid of a C_5H_5 ligand.

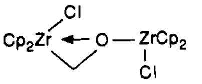
has also given us an opportunity to see how the structural properties of the trifluoroacetate ligand are affected by its reduction.

Results and Discussion

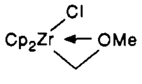
The final atomic coordinates of 8 and the equivalent isotropic thermal parameters for its non-hydrogen atoms are given in Table I. Selected bond lengths and angles are given in Table II. The structure of 8 and the numbering scheme used are shown in Figure 1. The final atomic coordinates of 9 and the isotropic thermal parameters for its non-hydrogen atoms are given in Table III. Selected bond lengths and angles are given in Table IV. The structure of 9 and the numbering scheme used are shown in Figure 2.

As expected, the benzyl carbon of 8 (C1), the nitrogen of its dimethylamino substituent (N1), and its trifluoroacetate oxygen (O1) lie approximately in the plane bisecting its CpZrCp unit. The trifluoroacetate oxygen O1 is only 0.19 Å out of the Zr1–C1–N1 plane, and the Zr1–C1–N1/C1–N1–O1 dihedral angle is only 5.1°. Similarly, the iminoacyl carbon (C21) and nitrogen (N1) of 9 and the oxygen (O2) of its diolate ligand lie approximately in a plane bisecting its Cp3Zr2Cp4 unit.

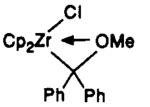
The nitrogens of the (dimethylamino)benzyl ligand in **8** and of the iminoacyl in **9** are coordinated inside. This result and the similar structures known for the nitrogen-containing **1** and **2** suggest that inside coordination is generally preferred when the coordinated heteroatom E is nitrogen. As far as we are aware, inside coordination is *invariably* more stable when E is oxygen: examples include the CH_2OZr ligand in $Cp_2Zr(Cl)CH_2OZr(Cl)Cp_2$ (**12**),[12a] the CH_2OCH_3 ligand in $Cp_2Zr(Cl)CH_2OCH_3$ (**13**),[12b]



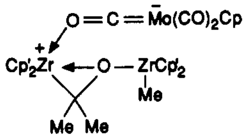
12



13



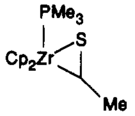
14



15

the CPh_2OCH_3 ligand in $Cp_2Zr(Cl)CPh_2OCH_3$ (**14**),[12c] the ethoxyethyl ligand in $Cp_2Zr(Cl)CH(CH_3)OCH_2CH_3$,[12d] the (benzyloxy)methyl ligand in $Cp_2Zr(Cl)CH_2OCH_2Ph$,[12e] the $C(CH_3)_2OZr$ ligand in **15**,[10] and numerous acyl and aroyl complexes[2] and aldehyde and ketone complexes.[9a,13]

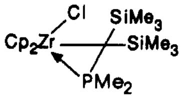
Inside coordination has also been found in the only X-ray structure of an η^2 structure with a sulfur-containing ligand (**16**).[14] NMR considerations have implied η^2



16

structures for several α-zirconocenyl thioethers,[14,15] and in one case the presence of a mixture of inside and outside isomers in solution has been suggested.[15]

When E is phosphorus η^2 structures are rare. However, the only such zirconocene derivative characterized by X-ray crystallography, **17**, has proven to have an outside



17

structure.[16] Furthermore, extended Hückel calculations indicate that the inside and outside forms of $Cp_2ZrCl(CH_2PH_2)$ are almost equal in energy.[17]

Similar calculations, however, indicate a preference for the inside isomer for acyl complexes of group 4 metals.[18] The structural results above, taken together, convince us that there must be some electronic preference for inside structures regardless of the identity of the coordinated heteroatom E. We believe that the occasional outside structures arise from steric effects—the picoline methyl in the η^2-picolyl cation **3** cannot point toward the PMe_3 ligand, and the two trimethylsilyl substituents in **17** must occupy the central coordination site in order to avoid interaction with the cyclopentadienyl rings. The fact that **14**, with its two phenyl substituents on the α-carbon, has an inside structure is impressive testimony to the size of the electronic preference for such structures.

Bond Lengths. The bond between Zr1 and the sp^3 carbon in **8** (C1) is the same length (2.297 (3) Å) as the $Zr-C(sp^3)$ bond in the similar compound **15** (2.302 (5) Å) and only slightly longer than the $Zr-C(sp^3)$ bond in **13** (2.271 (5) Å), but much shorter than the Zr–C bond in **14** (2.395 (6) Å). These Zr–C distances are easily explained by the steric effects of the substituents on the α-carbon (the distance decreases in the order $CPh_2 \gg CHPh \sim CMe_2 > CH_2$).[19]

However, the Zr1–C1 bond in **8** is *longer* than the bond between Zr and the sp^2 carbon in **9** (2.206 (5) Å) and the bond between Zr and the sp^2 (iminoacyl) carbon in **2** (2.247 (5) Å). The difference is roughly that predicted from the change in hybridization at carbon.[20]

The Zr1–N1 bond in **8** (2.312 (3) Å) is somewhat longer than would be expected from the Zr–O bond lengths in its oxygen analogues: the Zr–O bond in **13** is 2.204 (3) Å, and that in **14** is 2.215 (4) Å, while the covalent radius of the sp^3 nitrogen is only ~0.05 Å greater than that of the sp^3 oxygen.[21] It (the Zr1–N1 bond in **8**) is also surprisingly long in comparison with the Zr–N bonds of iminoacyls: the Zr–N bond in **2** is only 2.210 (4) Å and the Zr2–N1 bond in **9** is only 2.216 (4) Å, despite the fact that their Zr–C–N angles are similar (72.2 (2)° in **8** and 74.0 (3)° in **9**). Little of this difference is due to the change in hybridization at nitrogen between an aminoalkyl ligand (sp^3) and an iminoacyl one (sp^2): the covalent radius of the sp^3 nitrogen is only ~0.01 Å greater than the covalent radius of the sp^2 nitrogen.[22]

The C–N distances in **8** and **9** are slightly shorter than those found in organic compounds with the same C–N bond orders. The C1–N1 distance in **8**, 1.448 (5) Å, is slightly shorter than a typical organic C–N single bond (1.47 Å),[20] and the C21–N1 bond in **9** (1.255 (6) Å) is slightly shorter than a typical organic C=N double bond (1.28 Å).[20]

The distance between the zirconium and the trifluoroacetate oxygen in **8** (Zr1–O1 2.205 (3) Å) is very similar to that (2.217 (4) Å) found for the $Zr-(\eta^1)OC(O)CF_3$ bond in $[Cp_2Zr(OC(O)CF_3)(\mu\text{-}OH)]_2$.[23a] The Zr–O distances shorten considerably between the trifluoroacetate ligand

---

(12) (a) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690. (b) Erker, G.; Schlund, R.; Krüger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1403. (c) Erker, G.; Dorf, U.; Atwood, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 2251. (d) Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *Organometallics* **1988**, *7*, 2324. (e) Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *Organometallics* **1989**, *8*, 1593.

(13) See: (a) Erker, G.; Hoffmann, U.; Zwettler, R.; Betz, P.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 630. (b) Waymouth, R. W.; Potter, K. S.; Schaefer, W. P.; Grubbs, R. H. *Organometallics* **1990**, *9*, 2843 and references therein.

(14) Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 1590.

(15) Ward, A. S.; Mintz, E. A.; Ayers, M. R. *Organometallics* **1986**, *5*, 1585.

(16) Karsch, H. H.; Deubelly, B.; Hofmann, J.; Pieper, U.; Müller, G. *J. Am. Chem. Soc.* **1988**, *110*, 3654.

(17) Hofmann, P.; Stauffert, P.; Schore, N. E. *Chem. Ber.* **1982**, *115*, 2153.

(18) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440.

(19) The short $Zr-(sp^3)C$ distance reported in 12[12a] (2.19 (1) Å) is an exception to this pattern. However, other $Zr-CH_2$ bonds have the lengths expected from this series; e.g., $[Cp_2Zr(CH_3)]_2O$ has a Zr–C bond length of 2.266 (7) Å (Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Pentilla, R. E.; Atwood, J. L. *Organometallics* **1983**, *2*, 750).

(20) Standard bond length tables (Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1) show only 0.026 Å as the hybridization effect on each carbon when the $C(sp^3)-C(sp^3)$ bond length (1.530 Å) is compared with the $C(sp^2)-C(sp^2)$ bond length (1.478 Å, unconjugated). However, the same bond length tables show that changing carbon hybridization from sp^3 to sp^2 usually has a larger effect on C–X bonds; C–N bond lengths decrease by about 0.10 Å.

(21) Compare the $C(sp^3)-OH(sp^3)$ bond length (1.432 Å) with the $C(sp^3)-NH_3^+(sp^3)$ bond length (1.488 Å) in the tables in ref 20.

(22) Compare the $C(sp^3)-N(sp^2)$ bond lengths (an average of 1.463 Å) with the $C(sp^3)-N(sp^3)$ bond length (1.469 Å) in the tables in ref 20.

(23) (a) Klima, S.; Thewalt, U. *J. Organomet. Chem.* **1988**, *354*, 77. (b) Herrmann, G. S.; Alt, H. G.; Thewalt, U. *J. Organomet. Chem.* **1990**, *399*, 83.

in 8 and the reduced trifluoroacetate (*gem*-diolate) ligand in 9, with the Zr1–O1 distance in the latter (1.968 (3) Å) being even shorter than the Zr2–O2 distance (2.099 (3) Å). Both oxygens in 9 plainly serve as π donors, with Zr2 not being as good a π acceptor as Zr1 because the former has an extra nitrogen lone pair in its coordination sphere. The π-donor ability of an η^1-O_2CCF_3 ligand thus increases substantially when it is reduced to a *gem*-diolate ligand, in line with our suggestion some years ago[10] that η^1-O_2CCF_3 is a σ donor and not a π donor in zirconocene systems. Unreduced trifluoroacetate ligands are known to be sufficiently weak donors that they are unable to chelate in Ti and Zr metallocene systems.[23]

Experimental Section

All operations were performed under N_2 by Schlenk, vacuum line, and inert-atmosphere box techniques. Diethyl ether, pentane, and toluene were distilled under N_2 from sodium benzophenone ketyl, and hexane was treated with H_2SO_4 and then distilled from CaH_2. The ^1H NMR data were collected on a Bruker WP200 spectrometer; residual solvent proton shifts were used as internal standards. IR data were collected on a Perkin-Elmer 983 spectrophotometer. The methyl (dimethylamino)benzyl complex 7 was prepared from $Cp_2Zr(Me)Cl$[24] and PhCH(K)NMe_2[25] as reported elsewhere.[8] $Cp_2Zr(Me)H$ was prepared by the method of Jordan and co-workers.[26] The elemental analyses were performed by Analytische Laboratorien, Gummersbach, Germany.

$Cp_2Zr(O_2CCF_3)(\eta^2\text{-}CHPhNMe_2)$ (8). The methyl complex 7 (1.0 g, 2.7 mmol) was dissolved in 10 mL of toluene, and the solution was cooled to 0 °C. As this solution was stirred, 0.2 mL (0.3 g, 2.6 mmol) of CF_3CO_2H in 10 mL of toluene was added over 20 min. Stirring was continued for 20 min at 0 °C and for 20 min at 25 °C. The solvent was removed until the solution became cloudy (about 10 mL). A layer of hexane (1 mL) was added and the mixture cooled to −20 °C. The resulting precipitate was isolated by filtration (500 mg) and dried under vacuum; another 200 mg (for a total yield of 55%) was isolated after the filtrate was concentrated. Crystals suitable for an X-ray structure determination were grown out of a 10-mL of toluene/1 mL of hexane mixture; the crystals obtained (clear, colorless platelets) were not dried but were immediately mounted on the diffractometer in a stream of cold N_2. IR: (CH_2Cl_2) 1715 (vs), 1595 (w), 1488 (w), 1445 (w), 1406 (s) cm^{-1}; (KBr) 1690 (vs), 1595 (m), 1485 (w), 1441 (w), 1415 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.32–7.05 (m, 5 H, Ph), 6.11 (s, 5 H, Cp), 5.85 (s, 5 H, Cp), 3.76 (s, 1 H, CH), 2.83 (s, 3 H, NMe), 2.75 (s, 3 H, NMe). Anal. Calcd for $C_{21}H_{22}F_3NO_2Zr$: C, 53.82; H, 4.70; F, 12.17; N, 2.99. Found: C, 53.37; H, 4.72; F, 12.01; N, 2.94.

$Cp_2Zr(CMeN^tBu)(O_2CCF_3)$ (11). To a sample of $Cp_2ZrMe(O_2CCF_3)$ (10)[10] (150 mg, 0.43 mmol) in 40 mL of ether was added an excess of ^tBuNC. The solution was stirred at 25 °C for 12 h. Removal of volatiles left colorless, crystalline $Cp_2Zr(CMeN^tBu)(O_2CCF_3)$ in quantitative yield. IR (THF): 1702 (ν_{CO}), 1652 (ν_{CN}) cm^{-1}. ^1H NMR: (C_6D_6) δ 5.58 (s, Cp), 2.02 (s, Me), 1.04 (s, ^tBu); (CD_3CN) 5.86 (s, Cp), 2.75 (s, Me), 1.28 (s, ^tBu).

$Cp_2Zr(\eta^2\text{-}CMeN^tBu)(\mu\text{-}O,O'\text{-}O_2CHCF_3)Zr(Me)Cp_2$ (9). To a mixture of $Cp_2Zr(Me)H$ (219 mg, 0.924 mmol) and $Cp_2Zr(CMeN^tBu)(O_2CCF_3)$ (11) (400 mg, 0.926 mmol) was added 40 mL of THF. The suspension was stirred vigorously for 4 h at 25 °C while shielded from light. It was then filtered, the solvent was removed from the filtrate, and the resulting waxy crystals were triturated once with 5 mL of ether. Crystallization from 2 mL of ether/5 mL of pentane followed by a single wash with 5 mL of pentane yielded 526 mg of colorless crystals (85% yield). ^1H NMR (C_6D_6): δ 6.00, 5.93, 5.70, 5.64 (all s, Cp), 5.38 (q, J = 3.8 Hz, C*H*CF_3), 2.11 (s, C-*Me*), 1.20 (s, ^tBu), 0.50 (s, Zr-*Me*). ^{13}C NMR (C_6D_6): δ 237.1 (*C*=N^{t}Bu), 111.2, 110.6, 108.5, 108.4 (all *Cp*), 101.6 (q, J = 32.5 Hz, *C*F_3), 60.1 (*C*Me_3), 29.6 (C*Me*$_3$), 22.6, 21.5. Anal. Calcd for $C_{29}H_{36}F_3NO_2Zr_2$: C, 54.22; H, 6.02; N, 3.72. Found: C, 54.11; H, 5.92; N, 3.73.

Crystals of 9 were grown by slow evaporation from a saturated toluene solution at −20 °C in a refrigerator in an inert-atmosphere box. Crystals for X-ray study were mounted individually in 0.5-mm thin-walled glass capillaries under nitrogen.

Crystallographic Study of 8: crystal size 0.24 × 0.36 × 0.41 mm; $C_{21}H_{22}F_3NO_2Zr$; fw 468.22; monoclinic; space group $P2_1/n$; a = 8.839 (2) Å; b = 16.491 (4) Å; c = 13.887 (5) Å; β = 103.22 (2)°; V = 1971 (1) Å^3; Z = 4; D_x = 1.58 g cm^{-3}; λ(Mo Kα) = 0.7107 Å; μ = 5.84 cm^{-1}; T = −125 °C; F(000) = 952; Nicolet R3m diffractometer; unit cell constants from a least-squares fit of setting angles for 25 reflections ($2\theta_{av}$ = 14.02°). Data were collected ($\theta/2\theta$ scans) to $(\sin\theta)/\lambda$ = 0.5947 Å^{-1}, $0 \le h \le 11$, $0 \le k \le 20$, $-17 \le l \le 17$. Three standard reflections (200, 040, 002) were taken every 97 reflections. Lorentz and polarization corrections were made, but no absorption correction was applied due to the low absorption coefficient. There were a total of 3483 unique reflections; 2998 reflections with $F_o > 2.5\sigma(F_o)$ were observed.

The structure was solved by a Patterson map interpretation and refined by block diagonal (maximum 103 parameters/block, 259 parameters total, data/parameters = 11.58) weighted [$w = (\sigma^2(F) + gF^2)^{-1}$, $g = 5 \times 10^{-4}$] least-squares refinement on F. H atoms were placed in idealized positions (C–H = 0.96 Å, U(H) = 1.2 × U_{iso}(C)). The non-H atoms were refined with anisotropic thermal parameters. At convergence ($(\Delta/\sigma)_{max}$ = 0.019, $(\Delta/\sigma)_{mean}$ = 0.004 for last three cycles) R = 0.042, R_w = 0.053, S = 1.60, slope of normal probability plot = 1.29, $(\Delta\rho)_{max}$ = 0.63 e Å^{-3}, and $(\Delta\rho)_{min}$ = −0.55 e Å^{-3}. Neutral-atom scattering factors and anomalous dispersion corrections were used;[27] all calculations were performed using the SHELXTL program library.[28] Crystallographic data and results other than the final atomic coordinates and equivalent isotropic thermal parameters (Table I) appear as supplementary material.

Crystallographic Study of 9: crystal size 0.46 × 0.31 × 0.36 mm; $C_{29}H_{36}F_3NO_2Zr_2$; fw 670.05; space group $P2_1/n$; a = 12.085 (2) Å, b = 14.922 (3) Å, c = 15.927 (2) Å, β = 91.50 (1)°, V = 2871 (1) Å^3, Z = 4, D_x = 1.55 g cm^{-3}; λ(Mo Kα) = 0.7107 Å; μ = 7.49 cm^{-1}; T = −130 °C; F(000) = 1360; Nicolet R3m diffractometer; unit cell constants from a least-squares fit of setting angles for 25 reflections ($2\theta_{av}$ = 21.86°). Data were collected ($\theta/2\theta$ scans) to $(\sin\theta)/\lambda$ = 0.5947 Å^{-1}, $0 \le h \le 15$, $0 \le k \le 18$, $-19 \le l \le 19$. Three standard reflections (200, 060, 002) were taken every 97 reflections. Lorentz and polarization corrections were made, but no absorption correction was applied due to the low absorption coefficient. There were a total of 5015 unique reflections; 4615 reflections with $F_o > 2.5\sigma(F_o)$ were observed.

The structure was solved by a Patterson map interpretation followed by block diagonal (maximum 103 parameters/block, 320 parameters total, data/parameters = 14.42) weighted [$w = (\sigma^2(F) + gF^2)^{-1}$, $g = 5 \times 10^{-4}$] least-squares refinement on F. The *gem*-diol group and two of the Cp rings were disordered (see Figure 2); atoms of these groups were refined isotropically. Atoms of the *gem*-diol groups were refined and then constrained to site occupancy factors of 0.60 and 0.40, respectively. One of the Cp rings was refined and then constrained to a 0.65/0.35 disorder, and the other was refined and then constrained to a 0.70/0.30 disorder. No H atoms were added to this model due to the disorder. Nondisordered non-H atoms were refined with anisotropic thermal parameters. At convergence ($(\Delta/\sigma)_{max}$ = 0.090, $(\Delta/\sigma)_{mean}$ = 0.014 for last three cycles) R = 0.051, R_w = 0.077, S = 1.94, slope of normal probability plot = 1.50, $(\Delta\rho)_{max}$ = 0.74 e Å^{-3}, and $(\Delta\rho)_{min}$ = −0.80 e Å^{-3}. Neutron-atom scattering factors and anomalous dispersion corrections were used;[27] all calculations were performed using the SHELXTL program library.[28] Crystallographic data and results other than the final atomic coordinates and equivalent isotropic thermal parameters (Table III) appear as supplementary material.

Acknowledgment. We acknowledge the support of the National Science Foundation for the synthetic chemistry

---

[24] (a) Jordan, R. F. *J. Organomet. Chem.* **1985**, *294*, 321. (b) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729.

[25] Brandsma, L.; Verkruijsse, H. *Preparative Polar Organometallic Chemistry*; Springer: New York, 1987; Vol. 1, p 201.

[26] Jordan, R. F.; Bajgur, C. S.; Dasher, W. E.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1041.

[27] *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

[28] Sheldrick, G. M. SHELTXTL, Rev. 5; Nicolet XRD Corp.: Madison, WI, 1983.

Organometallics **1992**, *11*, 127-138

(Grant CHE-8819760) and for the purchase of the Nicolet R3m diffractometer and computing system. K.P. is also grateful to the Deutsche Forschungsgemeinschaft for financial assistance. We also thank E. K. Barefield for helpful discussions.

Registry No. **7**, 137365-76-5; **8**, 137365-77-6; **9**, 137393-39-6; **11**, 137365-78-7; CF_3CO_2H, 76-05-1; $Cp_2ZrMe(O_2CCF_3)$, 99494-55-0; ^{t}BuNC, 7188-38-7; $Cp_2Zr(Me)H$, 67659-92-1.

Supplementary Material Available: Lists of complete bond lengths and angles, anisotropic thermal parameters, and H coordinates for **8** and lists of complete bond lengths and angles and anisotropic and isotropic thermal parameters for **9** (26 pages); tables of structure factors for **8** and **9** (51 pages). Ordering information is given on any current masthead page.

Protonation of Diene Complexes of Rhodium, Iridium, Ruthenium, and Osmium: A Fine Balance between Terminal and Agostic Hydrides

Martin A. Bennett,* Ian J. McMahon, and Simon Pelling

Research School of Chemistry, Australian National University, GPO Box 4, Canberra, ACT 2601, Australia

Maurice Brookhart and David M. Lincoln

Department of Chemistry, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290

Received February 19, 1991

The structures of the cationic hydrido complexes formed on addition of HPF_6 to (η^5-pentamethylcyclopentadienyl)- and (η^6-arene)metal complexes containing various 1,3-dienes or 1,5-cyclooctadiene have been investigated by IR and NMR (^{1}H, ^{13}C) spectroscopy. The rhodium complexes $[RhH(\eta\text{-}C_5Me_5)(diene)]^+$ (diene = 1,3-cyclohexadiene (**1**), 2,3-dimethylbutadiene (**3**)) are highly fluxional η^3-enyl complexes with a M–H–C interaction (agostic hydrides), as shown by their ^{1}H and ^{13}C NMR spectra at −100 °C and by deuteration experiments. As with other compounds of this class, two reversible processes can be observed by variable-temperature NMR spectroscopy: (1) M–H bond cleavage to give a 16e η^3-enyl complex, which leads to exchange of the endo C–H bonds of **1** and exchange of the agostic methyl hydrogen atoms of **3**; (2) C–H bond cleavage to give a diene metal hydride, which, in combination with process 1, averages separately the endo and exo protons of **1** and the five dienyl protons of **3**. The free energy of activation ΔG^* for process 2 is slightly larger than for process 1, the estimated values being about 9.0 and 7.5 kcal/mol in the case of **3**. The complexes $[IrH(\eta\text{-}C_5Me_5)(diene)]^+$ (diene = 1,3-cyclohexadiene (**2**), 2,3-dimethylbutadiene (**4**)) and $[OsH(\eta\text{-}arene)(diene)]^+$ (arene = C_6H_6, diene = 1,3-cyclohexadiene (**5**), 2,3-dimethylbutadiene (**7**); arene = 1,3,5-$C_6H_3Me_3$, diene = 1,3-cyclohexadiene (**6**), 2,3-dimethylbutadiene (**8**)) are terminal hydrides in which the hydride ligand migrates between metal and diene reversibly and rapidly on the NMR time scale above room temperature ($\Delta G^* \simeq 12$ kcal/mol for **2** and **4**). The coupled ^{13}C NMR spectrum of $[RuH(\eta\text{-}C_6H_6)(C_6H_8)]^+$ (**9**) at −100 °C suggests that this compound contains an agostic hydride similar to **1** and **3**, but the ^{1}H and ^{13}C NMR spectra above −100 °C resemble those expected for a highly fluxional terminal hydrido diene complex, the free energy of activation ΔG^* for reversible Ru–H bond cleavage being 8.8 kcal/mol. In contrast to the rhodium complexes and most other agostic hydrides formed from protonation of diene complexes, therefore, ΔG^* for C–H bond cleavage (process 2) in **9** is less than that for M–H bond cleavage (process 1) and is probably about 5–6 kcal/mol. The compounds $[RuH(\eta\text{-}C_6Me_6)(C_6H_8)]^+$ (**10**) and $[RuH(\eta\text{-}arene)(1,3\text{-}diene)]^+$ (diene = 2,3-dimethylbutadiene, arene = C_6H_6 (**11**), $C_6H_3Me_3$ (**12**), C_6Me_6 (**13**); arene = C_6Me_6, diene = isoprene (**14**), 2-methyl-1,3-pentadiene (**15**), 3-methyl-1,3-pentadiene (**16**)) are also agostic, but in most cases limiting spectra cannot be obtained, even for process 1, at −100 °C. Protonation of M(η-arene)(1,5-COD) gives terminal hydrido diene complexes $[MH(\eta\text{-}arene)(1,5\text{-}COD)]^+$ (M = Ru, arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6; M = Os, arene = C_6H_6, $C_6H_3Me_3$). The compound obtained from $Ru(\eta\text{-}C_6Me_6)(1,5\text{-}COD)$ and DPF_6 incorporates deuterium at the methylene carbon atoms of the coordinated diene, which implies that $[RuH(\eta\text{-}C_6Me_6)(1,5\text{-}COD)]^+$ is in equilibrium with η^1,η^2-cyclooctenyl and possibly agostic η^3-cyclooctenyl species. All the protonated diene complexes except $[OsH(\eta\text{-}arene)(1,5\text{-}COD)]^+$ react with 2e-donor ligands (L) to give nonfluxional 18e complexes of the type $[M(\eta\text{-}C_5Me_5)(\eta^3\text{-}enyl)(L)]^+$ (M = Rh, Ir; L = *t*-BuNC) and $[M'(\eta\text{-}arene)(\eta^3\text{-}enyl)(L)]^+$ [M′ = Ru, Os; L = CO, *t*-BuNC, $P(OMe)_3$ (not all possible combinations)].

Introduction

Studies of the protonation of (1,3-diene)metal complexes have played an important part in the recognition of M–H–C (agostic) interactions.[1] In 1976 it was shown[2] that the ^{1}H and ^{13}C NMR spectra of protonated $Fe(CO)_3$(1,3-cyclohexadiene) are consistent with the agostic η^3-enyl structure **1**; such species are undoubtedly formed on protonation of all (1,3-diene)iron tricarbonyls, though they have never been isolated. Complexes of the type $Fe\{P\{(OMe)_3\}_3$(1,3-diene) and $[Mn(CO)_3(1,3\text{-}diene)]^-$ are more basic than the corresponding $Fe(CO)_3$(1,3-diene) compounds, and their monoprotonated derivatives can be isolated.[3,4] Neutron diffraction studies of the complexes

---

(1) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(2) Brookhart, M.; Whitesides, T. H.; Crockett, J. M. *Inorg. Chem.* **1976**, *15*, 1550.

0276-7333/92/2311-0127$03.00/0