determined by X-ray crystallography to be [PPN][$Fe_3(CO)_8(NO)(NH)$] (**3**). The remaining products showed absorption bands in CH_2Cl_2 at 1645 (s), 1710 (m), 1780 (m), 1880 (vs), and 1990 (s) cm^{-1}; although they were not fully characterized, the bands at 1645, 1880, and 1990 cm^{-1} suggest the presence of $[Fe(CO)_3(NO)]^-$ (1650, 1875, and 1980 cm^{-1}).

Figure 3 shows a view of the anion illustrating the atomic numbering scheme. The Fe_3 triangle is symmetrically capped with a μ_3-NH imido group. This overall geometry is very similar to that observed for $FeCo_2(CO)_9(NH)$[7] and to that advanced from mass spectrometry for $Fe_3(CO)_{10}(NH)$.[21] The three iron atoms form an approximately equilateral triangle with a short average bond length of 2.549 (1) Å, if compared to other μ_3-bridged Fe_3 clusters.[30] The bonding angle Fe(3)-N(2)-O(2) of 169.9 (5)°, the relatively low value of ν(NO) (1700 cm^{-1}) and the short Fe(3)-N(2) bond length (1.638 (6) Å) suggest[31] a rather strong back-bonding from Fe(3). Two semibridging interactions, Fe(2)-C(32) and Fe(1)-C(31) [Fe(3)-C(31)-O(31) = 165.3 (7)°, α = 0.45; Fe(3)-C(32)-O(32) = 164.8 (6)°, α = 0.39], compensate for the imbalanced charges on Fe(1) and Fe(3). The three Fe-N(1) bond distances (mean 1.872 (5) Å) are similar to that in $Fe_3(CO)_{10}(NSiMe_3)$[32] (1.899 Å) and in $FeCo_2(CO)_9(NH)$ (1.86 Å). Contrary to $Fe_3(CO)_{10}(NH)$ and $H_2Ru_3(CO)_9(NH)$,[2b] we did not observe any ^1H NMR signal from the imido hydrogen atom, probably because of lower symmetry and/or proton exchange with the solvent as observed in $[Fe_3(CO)_{10}(CH)]^-$.[33] However, the imido hydrogen atom has been located from a difference Fourier map at 0.87 (7) Å from N(1). This distance is very similar to the N-H in $FeCo_2(CO)_9$ (NH) (0.83 (3) Å). As for this latter compound, prepared from $[FeCo_3(CO)_{12}]^-$ and NO^+ in CH_2Cl_2, the origin of the imido hydrogen atom is puzzling. The surprisingly high yield of the reaction rules out the possibility of a protonation from residual water in CH_2Cl_2 or in $Fe(CO)_2(NO)_2$ (both have been dried over P_2O_5). We consider that this hydrogen atom has been abstracted from the solvent, which suggests highly basic intermediate species in the reaction schemes.

Registry No. **1**, 104716-28-1; **2**, 104738-06-9; **3**, 104716-30-5; $Fe_5C(CO)_{15}$, 11087-47-1; [PPN)[$Fe(CO)_3(NO)$], 61003-17-6; [PPh_4][$Fe(CO)_3NO$], 104716-31-6; $[PPN]_2[Fe_6C(CO)_{13}(NO)_2]$, 104716-33-8; $Fe(CO)_2(NO)_2$, 13682-74-1; $[PPN]_2[Fe_3(CO)_{11}]$, 66039-65-4; CH_2Cl_2, 75-09-2.

Supplementary Material Available: Listings of atomic coordinates, thermal parameters, bond lengths, and bond angles (27 pages); listing of structure factor amplitudes (96 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of [*cyclo*-$(PhAs)_6Mo(CO)_4$] Containing a 1,4-Bidentate Coordinated Cyclohexaarsine Ring in a Twisted Boat Conformation

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The crystal and molecular structure of [*cyclo*-$(PhAs)_6Mo(CO)_4$] has been determined: monoclinic, $P2_1/c$, a = 11.850 (3) Å, b = 15.085 (3) Å, c = 25.302 (9) Å, β = 115.75 (3)°, V = 4074 (2) $Å^3$, Z = 4, R_F = 4.16%, T = 295 K. The structure contains a 1,4-bidentate coordinated molecule of *cyclo*-$(AsPh)_6$ in a previously unknown twisted boat conformation. The overall complex possesses approximate C_2 symmetry. The boat conformation provides a short As···As separation (3.196 (1) Å) needed for complex formation. The structure of the complex is compared to that of its uncoordinated precursor, *cyclo*-$(PhAs)_6$, which crystallizes in a chair conformation.

Introduction

One of the most striking features of reactions of homoatomic cyclopolyphosphines and arsines, *cyclo*-$(RE)_n$, with metal carbonyls is the variety of ring and chain dimensions found in the products.[1] There is the appearance of a seemingly free ability of the group-15 rings either to expand or contract the number of catenated units and either to retain a cyclic structure or open to form chains. This freedom contrasts sharply with the high specificity found in the ring dimensions of the uncoordinated precursors; for a particular R group, usually only a single (occasionally two) stable ring size is known.[2] More familiar to most chemists is the eventual conversion of all sulfur allotropes to *cyclo*-S_8; in this comparison it may be noted that S and RE units are isolobal.

Nearly 20 years ago, West et al. reported the synthesis of [$(PhAs)_6Mo(CO)_4$] (I) from the combination of *cyclo*-$(PhAs)_6$ (II) and $Mo(CO)_6$.[3] They proposed a structure based on 1,3-ring coordination of the known chair conformation of uncoordinated *cyclo*-$(PhAs)_6$.[4] No confirming

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(1) (a) West, B. O. In *Homoatomic Rings, Chains and Macromolecules of Main-Group Elements*; Rheingold, A. L., Ed.; Elsevier: Amsterdam, 1977; p 409. (b) Rheingold, A. L.; Churchill, M. R. *J. Organomet. Chem.* **1983**, *243*, 165.

(2) (a) Mills, J. L. In ref 1a, p 349. (b) Smith, L. R.; Mills, J. L. *J. Organomet. Chem.* **1975**, *84*, 1.

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(4) (a) Hedberg, K.; Hughes, E. W.; Waser, J. *Acta Crystallogr.* **1961**, *14*, 369. (b) Rheingold, A. L.; Sullivan, P. J. *Organometallics* **1983**, *2*, 327.

0276-7333/86/2305-2410$01.50/0

Table I. Crystal, Data Collection, and Refinement Parameters for [*cyclo*-$(AsPh)_6Mo(CO)_4$] (I)

(a) Crystal Parameters (22 °C)			
formula	$C_{40}H_{30}As_6MoO_4$	V, Å^3	4074 (2)
crystal system	monoclinic	Z	4
space group	$P2_1/c$	μ(Mo Kα), cm^{-1}	51.8
a, Å	11.850 (3)	D(calcd), g cm^{-3}	1.826
b, Å	15.085 (3)	color	yellow
c, Å	25.302 (9)	size, mm	0.27 × 0.28 × 0.30
β, deg	115.75 (3)	T_{max}/T_{min}	0.63/0.45
(b) Data Collection			
diffractometer	Nicolet R3m/μ	rflns collected	5728
radiation	Mo Kα	unique rflns	5332
wavelength, Å	0.71073	R(int), %	2.1
scan limits, deg	$4 \leqslant 2\theta \leqslant 45$	rflns, $F_o \geqslant 3\sigma(F_o)$	3911
scan type	omega	std rflns	3 std/97 data (<1% decay)
scan speed, deg min^{-1}	var. 6–20		
(c) Refinement			
R_F, R_{wF}, %	4.16, 4.86	Δ/σ (final)	0.061
GOF	1.074	$\Delta(\rho)_{max}$, e Å^{-3}	0.70
N_o/N_v	8.7	g, $w^{-1} = \sigma^2(F_o) + gF_o^2$	0.001

crystallographic characterization for I was performed, but the structure of a related complex, [$(MeP)_6W(CO)_4$] (III), revealed 1,4-bidentate coordination of the cyclophosphine in a boat conformation.[5] We have repeated West's synthesis of I and have determined that the structure of I is similar to III.

Experimental Section

Synthesis of I. I was prepared by a modification of the method of Ang and West.[3] In a sealed heavy-wall cube, 4.59 g (5 mmol) of *cyclo*-$(PhAs)_6$ and 1.34 g (5 mmol) of $Mo(CO)_6$ were heated in 50 mL of a 1:1 toluene/diglyme solution at 130 °C for 1.5 h. On cooling, the solution was filtered and the solvent evaporated. Chromatography (alumina, 80:20 petroleum ether/ethyl acetate) gave a bright yellow solution from which an 8.5% yield of yellow, crystalline I was obtained following solvent evaporation: mp 195–197 °C (lit.[3] mp 200 °C); IR (CO) 2021, 1920, 1891 cm^{-1} (lit.[3] 2020, 1920, 1889 cm^{-1}).[3]

Structural Determination. Crystals of I suitable for a diffraction study were obtained from acetone recrystallization and were mounted on a glass fiber with epoxy cement. The space group was uniquely determined by systematic absences, and the unit-cell parameters were obtained from the least-squares fit of the angular settings of 25 reflections ($22° \leq 2\theta \leq 30°$). Table I gives the unit-cell parameters and the details of the data collection and refinement. The intensity data were corrected for Lp effects and for absorption (empirical, 216 data).

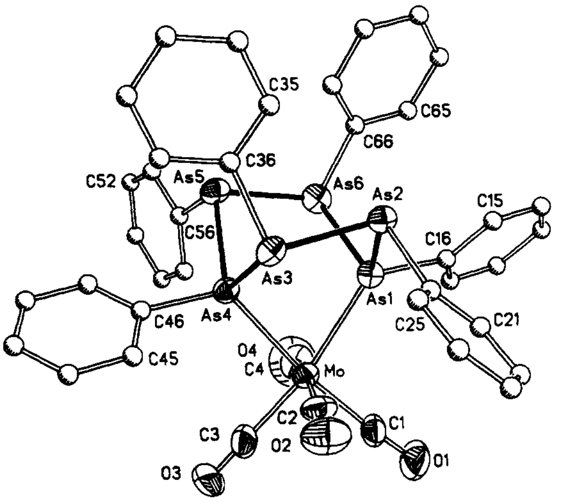

Figure 1. Molecular structure and labeling scheme for [*cyclo*-$(AsPh)_6Mo(CO)_4$] (I). The phenyl rings are depicted as arbitrarily sized spheres to minimize clutter.

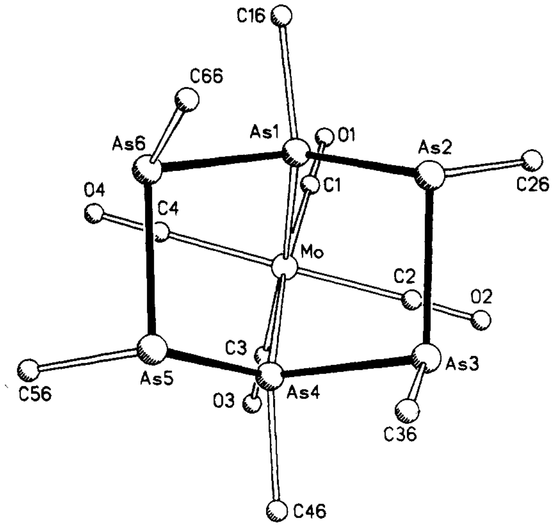

Figure 2. A view of I down the approximate twofold rotational symmetry axis. Phenyl rings shown as ipso atoms only.

The structure was solved by direct methods which located the seven heavy atoms; the remaining non-hydrogen atoms were obtained from subsequent difference Fourier syntheses. Blocked-cascade refinement with all non-hydrogen atoms anisotropic and all hydrogen atoms idealized isotropic contributions (d(C–H) = 0.96 Å, U = 0.08 Å^2) converged to the standard residuals in Table I. The phenyl rings were constrained to rigid, planar hexagonal groups (d(C–C) = 1.395 Å). The somewhat high thermal parameters associated with the outer carbon atoms of the C(51) to C(56) phenyl ring may be the result of unresolved positional disorder. No difference map peaks, however, were found that could be used to construct a sensible disorder model.

All computer programs and sources of neutral atom scattering factors are contained in the SHELXTL program library, Nicolet XRD Corp., Madison, WI. Table II gives the atomic coordinates and Table III selected molecular parameters. Additional crystallographic data are available as supplementary material (see note).

Results

[*cyclo*-$(PhAs)_6Mo(CO)_4$] (I) crystallizes as discrete molecules without significant intermolecular contacts. The structure is shown in Figures 1 and 2. The Mo atom coordination environment is distorted octahedral and typical of *cis*-$(CO)_4Mo$(L–L) complexes where L–L represents a chelating ligand with P or As donor atoms. The As–Mo–C and C–Mo–C bond angles reveal that the distortions to octahedral symmetry are largely manifested in a bending away of the $Mo(CO)_4$ group from the *cyclo*-$(AsPh)_6$ ligand. The Mo–C distances trans to As (1.97 (1) Å) are shorter than those trans to CO (2.03 (1) Å), in keeping with the comparative weakness of trivalent arsenic's π-acidity.

The cis-chelating ligand is a molecule of *cyclo*-$(PhAs)_6$ in an unusual twisted boat conformation. The average As–As bond distance, 2.454 Å, is very similar to that found in the uncomplexed ligand (II), 2.459 Å,[4b] which crystallizes

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[5] Elmes, P. S.; Gatehouse, B. M.; West, B. O. *J. Organomet. Chem.* **1974**, *82*, 235.

Table II. Atomic Coordinates ($\times 10^4$ Å) and Isotropic Temperature Factors (Å$^2 \times 10^3$) for [*cyclo*-$(AsPh)_6Mo(CO)_4$] (I)

atom	*x*	*y*	*z*	*U*,[a] Å^2
Mo	1863 (1)	7465 (1)	339 (1)	48 (1)
As(1)	2044 (1)	7174 (1)	1387 (1)	46 (1)
As(2)	3111 (1)	8289 (1)	2128 (1)	47 (1)
As(3)	4584 (1)	8704 (1)	1719 (1)	48 (1)
As(4)	4285 (1)	7474 (1)	1025 (1)	45 (1)
As(5)	5344 (1)	6308 (1)	1736 (1)	53 (1)
As(6)	3397 (1)	5865 (1)	1786 (1)	54 (1)
C(1)	30 (10)	7583 (8)	−60 (5)	67 (5)
C(2)	1890 (11)	8808 (8)	372 (4)	65 (6)
C(3)	2024 (10)	7577 (8)	−400 (6)	71 (6)
C(4)	1556 (11)	6159 (9)	144 (6)	80 (7)
O(1)	−1053 (7)	7647 (7)	−271 (4)	122 (5)
O(2)	1832 (9)	9567 (6)	322 (4)	107 (6)
O(3)	2103 (9)	7629 (7)	−839 (4)	119 (6)
O(4)	1289 (11)	5457 (7)	−25 (5)	150 (8)
C(11)	16 (8)	6011 (5)	1257 (3)	81 (7)
C(12)	−823 (8)	5585 (5)	1425 (3)	122 (11)
C(13)	−922 (8)	5853 (5)	1931 (3)	123 (12)
C(14)	−182 (8)	6547 (5)	2269 (3)	110 (10)
C(15)	657 (8)	6973 (5)	2102 (3)	78 (7)
C(16)	756 (8)	6705 (5)	1596 (3)	64 (6)
C(21)	659 (6)	9182 (4)	1491 (3)	77 (6)
C(22)	−120 (6)	9921 (4)	1286 (3)	96 (7)
C(23)	399 (6)	10766 (4)	1348 (3)	87 (7)
C(24)	1697 (6)	10873 (4)	1615 (3)	84 (8)
C(25)	2476 (6)	10135 (4)	1820 (3)	68 (6)
C(26)	1957 (6)	9289 (4)	1758 (3)	45 (5)
C(31)	7267 (8)	8404 (5)	2294 (3)	77 (6)
C(32)	8449 (8)	8383 (5)	2769 (3)	96 (8)
C(33)	8560 (8)	8410 (5)	3341 (3)	94 (7)
C(34)	7489 (8)	8459 (5)	3438 (3)	90 (7)
C(35)	6306 (8)	8481 (5)	2962 (3)	67 (6)
C(36)	6195 (8)	8453 (5)	2391 (3)	54 (5)
C(41)	6506 (7)	7335 (4)	804 (3)	77 (7)
C(42)	7363 (7)	7647 (4)	606 (3)	85 (7)
C(43)	7230 (7)	8498 (4)	370 (3)	83 (7)
C(44)	6240 (7)	9036 (4)	332 (3)	86 (7)
C(45)	5384 (7)	8724 (4)	531 (3)	72 (6)
C(46)	5517 (7)	7873 (4)	766 (3)	49 (5)
C(51)	6150 (6)	4639 (5)	1522 (3)	69 (6)
C(52)	6150 (6)	3859 (5)	1226 (3)	90 (8)
C(53)	5265 (6)	3737 (5)	647 (3)	117 (10)
C(54)	4381 (6)	4395 (5)	364 (3)	224 (14)
C(55)	4381 (6)	5176 (5)	660 (3)	208 (12)
C(56)	5266 (6)	5298 (5)	1239 (3)	59 (5)
C(61)	4905 (7)	6477 (5)	2999 (4)	68 (6)
C(62)	5145 (7)	6568 (5)	3587 (4)	89 (8)
C(63)	4318 (7)	6208 (5)	3787 (4)	112 (10)
C(64)	3250 (7)	5758 (5)	3400 (4)	107 (10)
C(65)	3010 (7)	5667 (5)	2811 (4)	77 (7)
C(66)	3838 (7)	6027 (5)	2611 (4)	56 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Distances, Bond Angles, and Torsion Angles for [*cyclo*-$(AsPh)_6Mo(CO)_4$] (I)

(a) Bond Distances (Å)

As(1)–As(2)	2.426 (1)	Mo–As(1)	2.604 (2)
As(2)–As(3)	2.465 (2)	Mo–As(4)	2.631 (1)
As(3)–As(4)	2.471 (1)	Mo–C(1)	1.97 (1)
As(4)–As(5)	2.438 (1)	Mo–C(2)	2.03 (1)
As(5)–As(6)	2.457 (2)	Mo–C(3)	1.97 (1)
As(6)–As(1)	2.466 (1)	Mo–C(4)	2.03 (1)
As–As(av)	2.454		

(b) Bond Angles (deg)

As(1)–As(2)–As(3)	94.5 (1)	As(1)–Mo–C(4)	90.6 (4)
As(2)–As(3)–As(4)	101.5 (1)	As(4)–Mo–C(1)	169.7 (4)
As(3)–As(4)–As(5)	98.5 (0)	As(4)–Mo–C(2)	88.5 (3)
As(4)–As(5)–As(6)	92.3 (1)	As(4)–Mo–C(3)	95.6 (3)
As(5)–As(6)–As(1)	102.7 (1)	As(4)–Mo–C(4)	101.2 (3)
As(6)–As(1)–As(2)	102.2 (0)	C(1)–Mo–C(2)	85.7 (5)
As–As–As(av)	98.6	C(1)–Mo–C(3)	92.6 (5)
As(1)–Mo–As(4)	75.3 (0)	C(1)–Mo–C(4)	85.5 (5)
As(2)–As(1)–Mo	117.0 (1)	C(2)–Mo–C(3)	87.0 (5)
As(6)–As(1)–Mo	107.7 (1)	C(2)–Mo–C(4)	168.6 (4)
As(3)–As(4)–Mo	104.5 (1)	C(3)–Mo–C(4)	86.2 (6)
As(5)–As(4)–Mo	123.2 (1)	Mo–C(1)–O(1)	177 (1)
As(1)–Mo–C(1)	97.0 (4)	Mo–C(2)–O(2)	172 (1)
As(1)–Mo–C(2)	97.7 (4)	Mo–C(3)–O(3)	179 (1)
As(1)–Mo–C(3)	169.6 (3)	Mo–C(4)–O(4)	172 (1)

(c) Torsion Angles (deg)

As(1)–As(2)–As(3)–As(4)	−13.3 (1)
As(2)–As(3)–As(4)–As(5)	−72.5 (1)
As(3)–As(4)–As(5)–As(6)	90.5 (1)
As(4)–As(5)–As(6)–As(1)	−18.7 (1)
As(5)–As(6)–As(1)–As(2)	−66.5 (1)
As(6)–As(1)–As(2)–As(3)	84.4 (1)

in the expected chair conformation. A greater range of As–As distances is found in I (2.426 (1)–2.471 (1) Å) in comparison to II (2.456 (1)–2.464 (1) Å),[4b] but since both the shortest, As(1)–As(2), and longest, As(3)–As(4), As–As bonds in I both contain metal-coordinated As atoms, no relationship to metal coordination is apparent. The As–As–As angles in I (average 98.6°) are much larger than in II (average 91.1), the minimum angle in I, As(4)–As(5)–As(6), is also larger than the average in II.[4b] Two of the three unique angles in II are actually slightly acute. As with the As–As distances, no pattern in the As–As–As angles related to metal coordination is discernible. In II, the 1,3-transannular contacts ranged from 3.446 (1) to 3.616 (1) Å;[4b] in I, the contacts are longer, ranging from As(4)···As(6) at 3.532 (1) Å to As(1)–As(5) at 3.844 (1) Å. However, the shortest As···As contact in I is the As(1)···As(4) distance of 3.196 (1) Å, a distance considerably shorter than any found in II, which may explain the inability of the chair conformation (as exists in II) to function as a bidentate ligand.

The overall structure is very similar to that found for [*cyclo*-$(MeP)_6W(CO)_4$] (III).[5] Crystallographically rigorous twofold symmetry exists in III and is approximately preserved in I. The view in Figure 2 looks down the approximate twofold axis. The pattern of the variation in the As–As distances and As–As–As angles is consistent with approximate C_2 molecular symmetry. The presence of related twofold symmetry in both I and III is more than coincidence; it represents the only solution to the uncrowded positioning of organic substituents while pyramidal As geometry is preserved in a boat conformation. It is only the phenyl ring plane orientations in I that significantly disrupts a closer approach to twofold symmetry. Another distortion, that of the difference in the Mo–As distances in I (Mo–As(1) = 2.604 (2) and Mo–As(4) = 2.631 (1) Å), is difficult to explain from an intramolecular perspective and probably results from intermolecular packing forces. The Mo–As distances are similar to several previously observed: in $[CpMo(CO)_2]_2$[μ-*catena*-$(CH_3As)_2$], the average Mo–As distance is 2.627 (1) Å.[1b]

Another structure related to both I and III is that found for [*cyclo*-$(PhPSi_2Me_4)_2Mo(CO)_4$] (IV) containing a regular boat conformation of a *cyclo*-1,4-diphospha-2,3,5,6-tetrasilahexane ring.[6]

Discussion

While it is attractive in its simplicity to propose that I forms by a direct dicarbonyl substitution mechanism involving only a ring-conformation change in the *cyclo*-$(AsPh)_6$ ligand, the probable course of events is likely more complex. Both I and III are formed under similar reaction conditions (1.5 h, 130 °C), yet the precursor to III is a

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(6) Calabrese, J. C.; Oakley, R. T.; West, R. *Can. J. Chem.* **1979**, *57*, 1909.

cyclopentamer, the only known stable methyl-substituted cyclooligomer, and requires a ring-expansion step. In reactions of *cyclo*-$(PhAs)_6$ with (arene)$Mo(CO)_3$ compounds under even milder conditions, the formation of {*cyclo*-$(PhAs)_9[Mo(CO)_3]_2$}, containing a nine-membered ring, proceeds in high yield.[7] The presence of six-membered rings in both I and its precursor is likely more coincidental than mechanistically informative.

Acknowledgment. The National Science Foundation provided assistance in the purchase of the diffractometer.

Supplementary Material Available: Tables of bond distances and angles, anisotropic temperature factors, and hydrogen atom coordinates (4 pages); a listing of observed and calculated structure factors (24 pages); Ordering information is given on any current masthead page.

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(7) Rheingold, A. L.; Fountain, M. E.; DiMaio, A.-J. *J. Am. Chem. Soc.*, in press.

The Reactivity of Complexed Carbocycles. 16.[1,2] Structural and NMR Spectroscopic Studies of Cyclooctatetraene as a Bridging Ligand: Five Different Bonding Modes in Dimetallic Complexes

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A series of dimetallic complexes have been prepared with cyclooctatetraene as a bridging ligand. An X-ray crystallographic analysis of $[C_5H_5Rh(C_8H_8)RhC_7H_8]BF_4$ (1) (C_7H_8 = norbornadiene), which crystallizes from acetone in the orthorhombic space group *Pnma* with $a = 18.611$ (2) Å, $b = 9.865$ (1) Å, $c = 9.899$ (1) Å, and $Z = 4$, reveals a cisoid $\eta^4{:}\eta^4$-bonding mode of the bridging ligand, similar to previously prepared compounds. On the other hand, $[(CO)_3Fe(C_8H_8)RhC_7H_8]BF_4$ (2), which crystallizes from acetone in the orthorhombic space group $P2_12_12_1$ with $a = 11.264$ (1) Å, $b = 11.681$ (1) Å, $c = 13.898$ (1) Å, and $Z = 4$, shows a different geometry for the bridging cyclooctatetraene with η^3(Fe)- and η^5(Rh)-coordination to the two metals. This difference is explained by two different modes of obtaining a closed shell for both metal atoms. A further series of cisoid complexes of general structure $[C_5H_5M_1(C_8H_8)M_2C_5R_5]^{n+}$ was prepared with $n = 0$–2 and R = H or CH_3. All complexes are fluxional on the ^{13}C NMR time scale. Complex 8 with $M_1 = M_2$ = Rh, R = H, and $n = 0$ was shown by X-ray structure analysis to contain a 1,2,6-η:3–5-η-bridging ligand with one uncoordinated double bond. This complex crystallizes from methylene chloride in the orthorhombic space group $P2_12_12_1$ with $a = 7.563$ (1) Å, $b = 11.239$ (2) Å, $c = 16.776$ (2) Å, and $Z = 4$. A general route to transoid dimetallic complexes having a pseudo-triple-decker structure has been developed. $C_5H_5Rh(C_8H_8)RhC_5H_5$ (11), an isomer of 8, crystallizes from chloroform/benzene in the monoclinic space group $P2_1/c$ with $a = 11.420$ (1) Å, $b = 28.410$ (3) Å, $c = 13.360$ (1) Å, $\beta = 92.76$ (1)°, and $Z = 12$. It shows a 1,2,5,6-η–3,4,7,8-η-coordination of tub-shaped C_8H_8 to the two rhodium centers; other complexes of this general type have indenyl or hexamethylbenzene ligands instead of cyclopentadienyl. A fifth type of coordination is found in $[C_5Me_5Rh(C_8H_8)CoC_5Me_5]^{2+}$ as well as $C_5H_5Ru(C_8H_8)RuC_5H_5$. These complexes have a slipped triple-decker structure with 1–5-η:4–8-η-transoid coordination in which two carbons of the bridging ring are simultaneously coordinated to both metal atoms. The ^{13}C NMR data of all complexes are reported, and the ^{103}Rh chemical shifts of selected mono- and dinuclear complexes are discussed.

Introduction

A large number of transition-metal complexes containing two metal centers are known.[4] The most common class involves metal–metal bonding between the same element, and complexes with two different metal centers are still relatively rare. This is largely due to difficulties in synthesis, since there are few reliable routes to such compounds. The most common methods produce mixtures of products or reduced yields due to competitive redox reactions between the two metals involved.

We had previously demonstrated that the low-valent, electron-rich cyclooctatetraene complexes CpM(COT) [Cp = cyclopentadienyl; COT = cyclooctatetraene; M = Co, Rh] and (COT)$Fe(CO)_3$ with two uncoordinated double bonds can be used as versatile starting materials for the synthesis of heterodimetallic complexes.[5a,b] This principle has also been extended to the preparation of dimetallic cycloheptatrienyl complexes.[6] On reaction with unsaturated 12e organometallic groups, these precursors yielded 34e species in high yields, in which both metals achieve a noble gas configuration through a metal–metal bond and a bridging fluxional carbocyclic ligand.

As the two metal moieties in our previously described dimetallic complexes, e.g., CpCo(COT)$Mo(CO)_3$ always differed by two electrons (CpCo, 14e; $Mo(CO)_3$, 12e), a closed-shell configuration for both metal centers could only

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