Acknowledgment. Financial support of this research through grants from the Department of Energy, Office of Basic Energy Sciences, and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. 2, 82583-10-6; **3**, 82583-08-2; **4**, 3910-35-8; **5**, 41906-71-2; $W(CO)_6$, 14040-11-0; $Mo(CO)_6$, 13939-06-5; *tert*-butylethylene, 558-37-2; tetramethylethylene, 563-79-1; 1,1-diphenylethylene, 530-48-3; poly(1,3-cyclohexadiene), 27986-50-1; poly(norbornadiene), 27859-77-4; quadricyclane, 278-06-8; norbornadiene, 121-46-0; polystyrene, 9003-53-6; poly(2-methylstyrene), 25014-31-7; 1,1,3-triphenyl-3-methylindan, 19303-32-3.

Structure and Bonding in a Phosphenium Ion–Iron Complex, $Fe[\eta^5-(CH_3)_5C_5](CO)_2[PN(CH_3)CH_2CH_2NCH_3]$. A Demonstration of Phosphenium Ion Acceptor Properties

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Summary: The combination of $NaFe[\eta^5-(CH_3)_5C_5](CO)_2$ with $CH_3NCH_2CH_2N(CH_3)PF$ in THF results in the formation of a metallophosphenium ion complex $Fe[\eta^5-(CH_3)_5C_5](CO)_2[PN(CH_3)CH_2CH_2NCH_3]$. The air-sensitive compound has been characterized by IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopies and single-crystal X-ray crystallography. The molecular structure contains a relatively long Fe–P bond distance, 2.340 (2) Å, and unlike other monometallic phosphenium ion complexes the geometry about the phosphorus atom is pyramidal instead of planar. The molecular structure is consistent with the cyclic phosphenium ion acting as an electron acceptor toward the electron-saturated $Fe[\eta^5-(CH_3)_5C_5](CO)_2^-$ fragment.

The interaction of selected aminohalophosphines with metal carbonyl anions leads to the heterolytic cleavage of the phosphorus–halogen bond and the formation of metallophosphenium ion complexes.[1-3] Molecular structure determinations for two compounds, $Mo(\eta^5-C_5H_5)(CO)_2[PN(CH_3)CH_2CH_2NCH_3]$ (**1**) and $Co_2(CO)_5[PN(CH_3)CH_2CH_2NCH_3]_2$ (**2**), have revealed that the cyclic phosphenium ion, $[PN(CH_3)CH_2CH_2NCH_3^+]$, may act as a terminal or bridging ligand,[2,3] and chemical properties and bonding analyses have suggested that $(R_2N)_2P^+$ species have both σ-donor and π-acceptor functionality.[2-6] In addition, intriguing similarities between phosphenium ions and carbenes,[7] SO_2,[8] and NO[9] have now become apparent. In this regard, we have briefly reported on the synthesis of a phosphenium ion–iron complex, $Fe(\eta^5-C_5H_5)(CO)_2[PN(CH_3)CH_2CH_2NCH_3]$ (**3**) from the combination of $NaFe(\eta^5-C_5H_5)(CO)_2$ and $CH_3NCH_2CH_2N(CH_3)PF$.[1] However, attempts to fully characterize **3** have been frustrated by decomposition reactions. We now wish to report the synthesis, characterization and crystal structure determination for the related complex $Fe[\eta^5-(CH_3)_5C_5](CO)_2[PN(CH_3)CH_2CH_2NCH_3]$ (**4**).[10]

Compound **4** was prepared by combination of $CH_3NCH_2CH_2N(CH_3)PF$[11] with an equimolar amount of $NaFeCp^*(CO)_2$[12,13] in tetrahydrofuran (THF). No CO was evolved, and a red, crystalline, air-sensitive solid was obtained.[15] The course of the reaction is summarized by eq 1. The absence of CO evolution suggests that the nature

$$CH_3NCH_2CH_2N(CH_3)PF + NaFeCp^*(CO)_2 \xrightarrow[25\ ^\circ C]{THF} NaF + \underset{\mathbf{4}}{CH_3NCH_2CH_2N(CH_3)PFeCp^*(CO)_2} \quad (1)$$

of the phosphenium ion interaction with the $FeCp^*(CO)_2^-$ fragment is uniquely different from the metal–phosphenium ion interactions in **1** and **2**.

The compound was initially characterized by elemental analysis and infrared and NMR spectroscopies.[15] A com-

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(1) Light, R. W.; Paine, R. T. *J. Am. Chem. Soc.* **1978**, *100*, 2230.

(2) Hutchins, L. D.; Paine, R. T.; Campana, C. F. *J. Am. Chem. Soc.* **1980**, *102*, 4521.

(3) Hutchins, L. D.; Light, R. W.; Paine, R. T. *Inorg. Chem.* **1982**, *21*, 266.

(4) Thomas, M. G.; Kopp, R. W.; Schultz, C. W.; Parry, R. W. *J. Am. Chem. Soc.* **1974**, *96*, 2646. Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1977**, *16*, 994.

(5) Montemayor, R. G.; Sauer, D. T.; Fleming, S.; Bennett, D. W.; Thomas, M. G.; Parry, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 2231. Bennett, D. W.; Parry, R. W. *Ibid.* **1979**, *101*, 755.

(6) Cowley, A. H.; Kemp, R. A.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 4289. Cowley, A. H.; Cushner, M. C.; Szobota, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 7784. Baxter, S. G.; Collins, R. L.; Cowley, A. H.; Sena, S. F. *Ibid.* **1981**, *103*, 714. Cowley, A. H.; Cushner, M. C.; Lattman, M.; McKee, M. L.; Szobota, J. S.; Wilburn, J. C. *Pure Appl. Chem.* **1980**, *52*, 789.

(7) The chemistry, structures, and bonding in metal carbene complexes have been described in several recent reviews: Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545. Cotton, F. A.; Lukehart, C. M. *Prog. Inorg. Chem.* **1972**, *16*, 487. Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1. Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1.

(8) The structures and bonding in metal–SO_2 complexes have been recently reviewed: Ryan, R. R.; Kubas, G. J.; Moody, D. C.; Eller, P. G. *Struct. Bonding (Berlin)* **1981**, *46*, 47.

(9) The structures and bonding in metal-nitrosyl complexes have been reviewed: Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339. Eisenberg, R.; Meyer, C. D. *Acc. Chem. Res.* **1975**, *8*, 26.

(10) Several reports of $CpFe(CO)_2(carbene)^+$ complexes have appeared, and representative examples are described in the following references: Fischer, E. O.; Kreis, G.; Kreissel, F. R.; Kreiter, C. G.; Muller, J. *Chem. Ber.* **1973**, *106*, 3910. McCormick, F. B.; Angelici, R. J. *Inorg. Chem.* **1979**, *18*, 1231. McCormick, F. B.; Angelici, R. J. *Ibid.* **1981**, *20*, 1111 and additional references can be found in ref 7. The formation of monometallic $FeCp(CO)_2SO_2^{0,\pm1}$ compounds has not been reported; however, bimetallic complexes $[FeCp(CO)_2]_2SO_2$ and $[FeCp(CO)]_2(CO)(SO_2)$ have been described: Churchill, M. R.; DeBoer, B. G.; Kalra, K. L. *Inorg. Chem.* **1973**, *12*, 1649. Churchill, M. R.; Kalra, K. L. *Ibid.* 1650.

(11) Fleming, S.; Lupton, M. K.; Jekot, K. *Inorg. Chem.* **1972**, *11*, 2534.

(12) Abbreviations used in the text include tetrahydrofuran, THF and pentamethylcyclopentadienide, Cp*.

(13) $NaFeCp^*(CO)_2$ was prepared by Na/Hg amalgam reduction of $[FeCp^*(CO)_2]_2$[14] in THF solution.

(14) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287.

(15) Compound **4** was isolated under inert-atmosphere conditions by filtration of the reaction mixture followed by vacuum evaporation of the THF filtrate. The evaporate was extracted with benzene and filtered, and a red solid (**4**) was recovered by vacuum evaporation of the benzene filtrate. The yield was 90%. Sublimation (65 °C (10^{-3} torr)) resulted in the recovery of pure, crystalline product: IR (carbonyl region, Nujol) 2002 (m), 1969 (s), 1954 (s), 1914 (s) cm^{-1}; NMR (32 °C, benzene) ^1H δ 3.07 (m, phosphenium ion methylene), 2.63 (d, $^3J_{HCNP} = 13.3$ Hz, phosphenium ion methyl), 1.67 (Cp* methyl), $^{13}C\{^1H\}$, δ 217.9 (d, $^2J_{CFeP} = 3.0$ Hz, carbonyls), 95.89 (Cp* ring), 54.78 (d, $^2J_{CNP} = 10.1$ Hz, phosphenium ion methylene), 35.23 (d, $^2J_{CNP} = 21.3$ Hz, phosphenium ion methyl), 9.31 ($^3J_{CCFeP} = 10.3$ Hz, Cp* methyl), $^{31}P\{^1H\}$ (85% H_3PO_4 standard), δ 285.9 (phosphenium ion phosphorus). Anal. Calcd for $FePO_2N_2C_{16}H_{25}$: Fe 15.3; P, 8.5; O, 8.8; N, 7.7; C, 52.8; H, 6.9. Found: Fe, 14.7; P, 8.1; O, 10.8; N, 7.5; C, 51.6; H, 6.8.

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plex, $FeCp^*(CO)_2L$, would be expected to show two bands in the terminal carbonyl stretching region. However, a Nujol mull of **4** unexpectedly displays six bands in the carbonyl region. Two weak absorptions at 1929 and 1747 cm^{-1} are coincident with absorptions from $[FeCp^*(CO)_2]_2$, and the remaining four bands at 2002, 1969, 1954, and 1914 cm^{-1} may be tentatively assigned to two rotational isomers of **4**. Similar results have been reported previously for $FeCp(CO)_2X$ compounds where X introduces asymmetry along the Fe–X bond axis.[16] Examinations of solution-phase infrared spectra of **4** are in progress.

The ^1H and $^{13}C\{^1H\}$ NMR spectra have been completely assigned,[15] and the data are consistent with the proposed formulation of **4**. The $^{31}P\{^1H\}$ spectrum shows a sharp singlet at 285.9 ppm which compares favorably with the shifts observed for **1** (271.5 ppm)[2] and **2** (307 ppm).[3] The large downfield ^{31}P shifts from the neutral ligand $CH_3\overline{NCH_2CH_2N(CH_3)P}F$ resonance (δ 138) and loss of P–F coupling are believed to be diagnostic of the formation of phosphenium ions or metallophosphenium ion complexes.[1-6] Evidence for rotational isomers has not been found in the ^1H or ^{13}C NMR spectra recorded at 30 °C. This observation is in accord with NMR studies of several $FeCp(CO)_2X$ complexes which display rotomers in their infrared spectra.[17] Apparently, rotation about the Fe–X bond is rapid on the NMR time scale, and separate resonances for the isomers are not detected. Low-temperature NMR studies of **4** are planned.

A X-ray crystal structure determination[18,19] of **4** verifies the composition as $Fe[\eta^5\text{-}(CH_3)_5C_5](CO)_2[\overline{PN(CH_3)CH_2CH_2N}CH_3]$, and a view of the molecular structure is shown in Figure 1. The iron atom is bonded to a planar Cp* ring in an η^5 fashion with Fe–C(ring)(av) = 2.136 (8) Å, C(ring)–C(ring)(av) = 1.409 (11) Å, and C(ring)–CH_3(av) = 1.512 (6) Å.[19] These distances compare with related distances in $FeCp^*_2$ (**5**), Fe–C(ring)(av) = 2.050 (2) Å, C(ring)–C(ring)(av) = 1.419 (2) Å, and C(ring)–CH_3(av) = 1.502 (3) Å,[20] in $FeCp^*(CO)_2SO_2CH_2CH{=}CH(C_6H_5)$ (**6**), Fe–C(ring)(av) = 2.115 (16) Å, C(ring)–C(ring)(av) = 1.431 (30) Å, and C(ring)–CH_3(av) = 1.509 (15) Å,[21] and in $[FeCp^*(CO)_2]_2$ (**7**), Fe–C(ring)(av) = 2.144 (9) Å, C(ring)–C(ring)(av) = 1.427 (2) Å, and C(ring)–CH_3(av) = 1.498 (2) Å.[22] The Cp* methyl groups in **4** are bent out of the ring plane and away from the Fe atom with methyl carbon atom deviations of 0.063–0.187 Å.[19] The iron atom is also bonded to two terminal CO ligands with Fe–CO(av) = 1.731 (7) Å and C≡O(av) = 1.158 (8) Å. These distances compare with the related distances in **6**, Fe–CO(av) = 1.766 (7) Å and C≡O(av) = 1.145 (14) Å, and in **7**, Fe–CO(av) = 1.753 (3) Å and C≡O(av) = 1.154 (3) Å. The C(11)–Fe–C(12) angle in **4**, 94.2 (3)°, is slightly more closed than the corresponding angle in **6**, 97.9 (4)°.

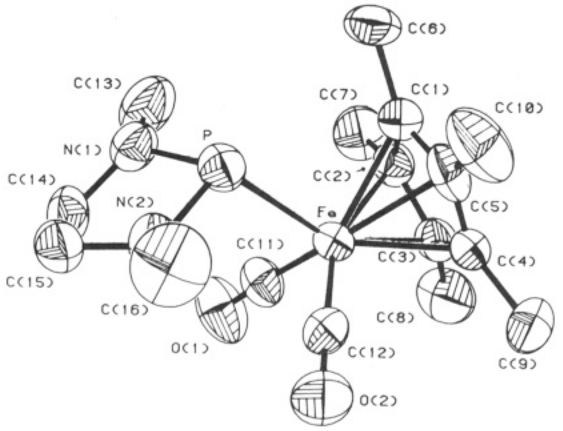

Figure 1. Molecular geometry and atom-labeling scheme for $Fe[\eta^5\text{-}(CH_3)_5](CO)_2[\overline{PN(CH_3)CH_2CH_2N}CH_3]$.

The structure of the iron atom–phosphenium ion fragment is of primary interest. The geometry about the phosphorus atom is clearly pyramidal with Fe–P = 2.340 (2) Å, P–N(av) = 1.701 (6) Å, Fe–P–N(1) = 114.8 (2)°, Fe–P–N(2) = 109.4 (2)°, and N(1)–P–N(2) = 89.3 (3)°. The Fe–P bond distance is long compared to the usual range associated with Fe–P bonds which contain both a dative P→Fe σ-bonding component and a Fe→P π-back-bonding component.[23] The Fe–P distance in **4** is similar to the distance in $Fe(CO)_4[(t\text{-}Bu)_3P]$, 2.364 (1) Å,[24] and the latter Fe–P bond is considered to have only a weak P→Fe σ dative bond. The P–N bond lengths in **4** are considerably longer than the distances found in **1**, 1.641 (5) and 1.650 (5) Å, **2**, 1.637 (5)–1.664 (4) Å, $[(i\text{-}Pr_2N)_2P^+][AlCl_4^-]$, 1.613 Å,[6] and the neutral phosphine ligand complex $Fe(CO)_4[CH_3\overline{NCH_2CH_2N(CH_3)P}F]$, 1.635 (5) and 1.642 (5) Å.[25] In **1**, the entire unit $CH_3\overline{NCH_2CH_2N(CH_3)P}Mo$ is planar, and this plane bisects the $Mo(CO)_2$ plane. In **4**, on the other hand, the unit $CH_3\overline{NCH_2CH_2N(CH_3)P}Fe$ is pyramidal about the phosphorus atom, and the phosphenium ion ring is bent toward the two CO ligands. Viewing down the P–Fe axis, the P–N and Fe–CO bonds approach an eclipsed configuration (torsion angle ~24°). The nitrogen atom geometry is approximately trigonal planar; however, the phosphenium ion ring is puckered so that the methyl and methylene carbon atoms on N(1) are below the PN_2 plane and those on N(2) are above the PN_2 plane.

On the basis of the molecular structures, the bonding in **4** must be distinctly different from the bonding in **1**. In **1**,[2] the planarity of the $CH_3\overline{NCH_2CH_2N(CH_3)P}Mo$ fragment, the short Mo–P bond distance and the slightly elongated P–N bond distances were used as evidence for the operation of synergic P lone pair ($8a_1$) to Mo atom σ donation and Mo atom to P ($4b_1$) back-donation interactions between the phosphenium ion and the formal 16-electron fragment $MoCp(CO)_2^-$.[26] In **4**, the pyramidal geometry requires a rehybridization (sp^2 to sp^3) of the phosphorus atom. This geometry and the quite long Fe–P and P–N bond lengths are consistent with electron dona-

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[16] (a) Jetz, W.; Graham, W. A. G. *J. Am. Chem. Soc.* **1967**, *89*, 2773. (b) Stanley, K.; Baird, M. C. *Ibid.* **1975**, *97*, 429. (c) Butler, I. S.; Sawai, T. *Inorg. Chem.*, **1973**, *12*, 1994. (d) Stanley, K.; Zelonka, R. A.; Thomson, J.; Fiess, P.; Baird, M. C. *Can. J. Chem.* **1974**, *52*, 1781.

[17] For example, see references given in reg 16b.

[18] Compound **4** crystallizes in the orthorhombic space group $P2_12_12_1$ with lattice constants a = 7.914 (1) Å, b = 8.832 (1) Å, c = 26.308 (3) Å, Z = 4, V = 1838.9 (4) $Å^3$, and ρ_{calcd} = 1.31 g cm^{-3}. Diffraction data were collected on a Syntex P3/F diffractometer by using Mo Kα radiation at 30 °C. The structure was solved by direct methods on 1416 independent reflections with $I \geq 2.5\sigma(I)$. The structure was refined anisotropically on all nonhydrogen atoms (isotropic on hydrogen atoms), and the final discrepancy indices were R_F = 0.045 and R_{wF} = 0.042.[19]

[19] Supplementary material: a full description of the structure solution appears in these materials along with tables of observed and calculated structure factors, non-hydrogen atom positional parameters, anisotropic thermal parameters, hydrogen atom positional parameters, a full listing of bond distances and angles, and least-squares planes calculations.

[20] Freyberg, D. P.; Robbins, J. L.; Raymond, K. N.; Smart, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 892.

[21] Churchill, M. R.; Wormald, J. *Inorg. Chem.* **1971**, *10*, 572.

[22] Teller, R. G.; Williams, J. M. *Inorg. Chem.* **1980**, *19*, 2770.

[23] Corbridge, D. E. C. "The Structural Chemistry of Phosphorus"; Elsevier: Amsterdam, 1974.

[24] Pickardt, J.; Rosch, L.; Schumann, H. *J. Organomet. Chem.* **1976**, *107*, 241.

[25] Bennett, D. W.; Neustadt, R. J.; Parry, R. W.; Cagle, F. W. *Acta Crystallogr., Sect. B* **1978**, *B34*, 3362.

tion from the 18-electron $FeCp^*(CO)_2^-$ fragment to the vacant LUMO ($4b_1$) on the phosphenium ion.[27] The phosphorus atom lone pair is no longer considered to be significantly involved in σ donation to the iron atom unit, and consequently, the lone pair should be stereochemically active.

Hoffmann and co-workers[28] have examined in detail the bonding in $MCp(CO)_2L$ complexes. When M = Fe the conceptual approach has involved the combination of metal orbitals on the 16-electron fragment $FeCp(CO)_2^+$ with ligand MOs having only σ donation (lone pair) or both σ donation and π back-donation ability. The formation of complexes from the combination of a filled metal orbital ($3a'$) on the 18-electron fragment $FeCp(CO)_2^-$ with ligand MOs having only electron accepting or both σ donor and π-acceptor character was not considered.[29] Compound 4 offers an ideal example of the latter case. It is expected in 4 that electron donation from the occupied iron $3a'$ orbital, which is primarily $3d_{z^2}$ in character, to an empty phosphenium ion three center MO ($4b_1$) which is antibonding with respect to the P–N bonds would result in a relatively weak Fe–P interaction and elongated P–N bonds. This is the trend observed in the structural parameters, and detailed MO calculations for 4 are in progress.

Finally, it is important to note that the structure of 4 is exactly that which would be predicted for the presently unknown complex $FeCp(CO)_2SO_2$. Other parallels between metallophosphenium ion complexes and metal–SO_2 complexes also are currently of interest.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. We also acknowledge NSF Grants CHE-7802921 and MPS-06111 which facilitated the purchase of the X-ray diffractometer and the NMR data system. We also wish to recognize continuing fruitful discussions and collaborations with R. R. Ryan and D. C. Moody of Los Alamos National Laboratory over the SO_2 analogy.

Registry No. 4, 82621-27-0; $CH_3\overline{NCH_2CH_2N(CH_3)P}F$, 33672-91-2; $NaFeCp^*(CO)_2$, 82621-26-9.

Supplementary Material Available: A listing of observed and calculated structure factors, positional parameters, anisotropic thermal parameters, bond distances and angles, and least-squares planes (20 pages). Ordering information is given on any current masthead page.

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(26) The important starting planar phosphenium ion orbitals in order of increasing energy are $3b_1$, out-of-plane three-center bonding MO delocalized over the PN_2 unit (occupied), $8a_1$, in-plane MO predominantly phosphorus lone pair in character (occupied), $4a_2$ out-of-plane ligand HOMO predominantly nitrogen lone pair in character (occupied), and $4b_1$, out-of-plane ligand LUMO delocalized over the PN_2 unit (unoccupied). In 1, the $P \rightarrow Mo$ σ donation primarily involves overlap of the ligand $8a_1$ MO and the metal d_{z^2} orbital, and the $Mo \rightarrow P$ π back-donation involves the overlap of the ligand $4b_1$ LUMO and the metal d_{xz} orbital.[2]

(27) Rehybridization of the phosphenium ion will not drastically affect the frontier orbital arrangement of the ligand. It is anticipated that the lone pair will occupy one sp^3 lobe and it should possess more p character than the $8a_1$ MO in the planar ligand. The LUMO ($4b_1$) in the planar ligand will remain as the LUMO in the pyramidal ligand and to a first approximation the orbital will have more s character than in the planar case. The ligand puckering is probably a response to the nitrogen atoms distorting in an attempt to retain the delocalized three-center N–P–N character in the LUMO ($4b_1$).

(28) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

(29) $CpFe(CO)_2^-$ may be conceptually formed by electron pair addition into the $3a'$ LUMO of $CpFe(CO)_2^+$. This MO is predominantly d_{z^2} in character.

A New Member of the $(HRhL_2)_x$ Cluster Class: $[(\mu\text{-H})Rh(1,5\text{-cyclooctadiene})]_4$

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Summary: Reaction of ethyllithium with $[(\mu\text{-Cl})Rh(1,5\text{-cyclooctadiene})]_2$ in diethyl ether at ~−80 °C forms $[(\mu\text{-}C_2H_5)Rh(1,5\text{-cyclooctadiene})]_2$. This dinuclear species is thermally reactive and through a series of β-hydride elimination and dissociation steps yields $[(\mu\text{-H})Rh(1,5\text{-cyclooctadiene})]_4$. This cluster is formally related to the $(HRhL_2)_x$ cluster group defined for a dimer and trimer.

Polynuclear rhodium and iridium complexes have resulted from the reaction of $[(\mu\text{-Cl})M(1,5\text{-cyclooctadiene})]_2$ with alkyl-, aryl-, and aralkyllithium reagents.[1] One of these products, the novel $[(\mu\text{-H})Rh(1,5\text{-cyclooctadiene})]_4$ cluster, 1, is described here in terms of structure, dynamic stereochemistry, and chemistry. Formally, this new cluster is related to the coordinately unsaturated group of $[HRh(PY_3)_2]_x$ clusters[2] initially described by us.[3–6] This structural class, rigorously established by X-ray and neutron diffraction studies[4,5,7,8] of a dimer and trimer, is characterized by a local, nearly coplanar, four-coordinate geometry (L_2RhH_2) for each rhodium atom. A projected structure[4] for the tetramer in this class was a puckered four-membered Rh_4 ring. In fact, the new $[(\mu\text{-H})Rh(1,5\text{-cyclooctadiene})]_4$ cluster can be described in these terms (or as a conventional tetrahedral cluster).

Single crystals[9] of the toluene solvate of $H_4Rh_4(1,5\text{-}C_8H_{12})_4$, 1, were, at 20 ± 1 °C, orthorhombic of space group $C222_1$—C_2^5 (No. 20) with $a = 10.939$ (2) Å, $b = 19.285$ (5) Å, $c = 31.548$ (8) Å, and $Z = 8$ $[H_4Rh_4(C_8H_{12})_4 \cdot 0.5CH_3C_6H_5]$ formula units ($d_{\text{calcd}} = 1.791$ g cm^{-3}; μ_a (Mo K$\bar{\alpha}$) = 1.91 mm^{-1}). Three-dimensional X-ray diffraction data were collected for 8182 independent reflections having $2\theta_{\text{MoK}\bar{\alpha}} < 71°$ (the equivalent of 2.0 limiting Cu K$\bar{\alpha}$ spheres) on a Nicolet P$\bar{1}$ autodiffractometer using graphite-monochromated Mo K$\bar{\alpha}$ radiation and full (1° wide) ω scans. The four rhodium atoms were located by using "direct methods" techniques and the remaining non-hydrogen and hydride hydrogen atoms with difference Fourier techniques; positions for cyclooctadiene hydrogen atoms were

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(1) Schmidt, G. F.; Muetterties, E. L.; Beno, M. A.; Williams, J. M. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1318.

(2) Y = OR, F, and $N(CH_3)_2$.

(3) Sivak, A. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 4878.

(4) Brown, R. K.; Williams, J. M.; Sivak, A. J.; Muetterties, E. L. *Inorg. Chem.* **1980**, *19*, 370.

(5) Teller, R. G.; Williams, J. M.; Koetzle, T. F.; Burch, R. R.; Gavin, R. M.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 1806.

(6) Meier, E. B.; Burch, R. R.; Muetterties, E. L.; *J. Am. Chem. Soc.* **1982**, *104*, 2661.

(7) Day, V. W.; Fredrich, M. F.; Reddy, G. S.; Sivak, A. J.; Pretzer, W. R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 8091.

(8) Brown, R. K.; Williams, J. M.; Fredrich, M. F.; Day, V. W.; Sivak, A. J.; Muetterties, E. L. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 2099.

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