$(PPh_3)^+Cl^-$ and $CpRu(CO)(PPh_3)Cl$[13] were formed as the only products in a ratio of 1:2, respectively (determined in CD_3NO_2 solution after completion of reaction). The ionic chloride **2d** showed no conversion to the covalent chloride **3d** under these conditions, but hydride **3b** was rapidly converted to this product after brief exposure to $CDCl_3$ at 50 °C. Thus two reaction paths are available to this acid: (a) decarboxylation followed by reaction of the hydride with the solvent or (b) direct reaction with the solvent.

The ionic products formed in the reactions conducted in chlorinated solvents result from redox processes. The ease of oxidation of both acids is evidenced by their rapid conversion to the corresponding cations $CpM(CO)_2(PPh_3)^+$ (M = Fe, Ru), by treatment with a catalytic amount of $AgBF_4$.[14] Thus, the reactions of **1a,b** appear to parallel the behavior of $CpFe(CO)(PPh_3)CH_3$ and related complexes in the presence of oxidizing agents; such alkyl complexes are converted to cation radicals by the action of catalytic amounts of $AgBF_4$ or $Ph_3C^+BF_4^-$.[15,16] Since cation radicals formed from organic carboxylic acids in mass spectrometers fragment in part by loss of ·OH to leave an acylium ion,[17] a similar fragmentation path may be expected for cation radicals formed from metallocarboxylic acids. The single product resulting from reactions of the iron acid with chlorinated solvents presumably reflects a lower ionization potential for **1a** in comparison to **1b** as expected.[18]

Work is in progress to establish other reaction characteristics of these two metallocarboxylic acids.

Acknowledgment. We are grateful to The Academic Excellence Commission, the Graduate Research Council, and the Arts and Sciences Research Committee of the University of Louisville for support of this work.

Registry No. **1a**, 70196-11-1; **1b**, 92670-59-2; **2a**, 32614-25-8; **2b**, 57327-09-0; **2c**, 12100-38-8; **2d**, 92670-60-5; **3a**, 32660-22-3; **3b**, 57327-06-7; **3d**, 32613-25-5; **4**, 12154-95-9; **5**, 60909-85-5; **6**, 35913-82-7; $CpFe(CO)_2Cl$, 12107-04-9.

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(13) Identified by spectral comparison with an authentic sample (Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2376).

(14) Although strong acids promote ionization of both **1a** and **1b**, stoichiometric quantities are needed to effect complete ionization. Also, **1a** and **1b** do not ionize upon standing in acetone solution for short periods of time although more polar solvents do cause ionization (see ref 2c).

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Synthesis and Structure of a Bimetallic Iron Carbonyl–Diazadiphosphetidine Complex, $Fe_2(CO)_8[P_2(t\text{-}BuN)_2(H)_2]$

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Summary: The reaction of $Na_2Fe(CO)_4\cdot{}^3/_2$dioxane with cyclic ClPN(*t*-Bu)P(Cl)N(*t*-Bu) in a 1:2 ratio in THF or Et_2O results in the formation of $Fe(CO)_4$[(H)PN(*t*-Bu)(P(H)N(*t*-Bu)]$Fe(CO)_4$. The structure of this unexpected complex has been determined by X-ray diffraction techniques and found to contain the previously unknown cyclic four-membered diazadiphosphetidine ring (H)PN(*t*-Bu)P(H)N-(*t*-Bu) with each phosphorus atom bonded to a $Fe(CO)_4$ fragment.

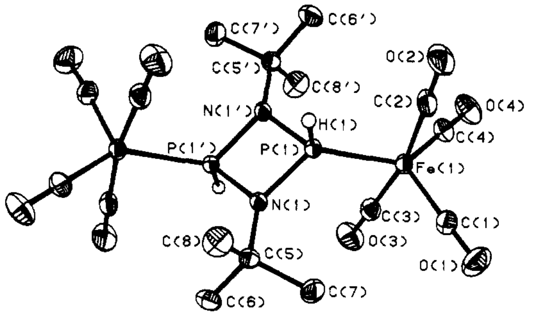

Figure 1. Molecular geometry and atom labeling scheme for $Fe_2(CO)_8$[(H)PN(*t*-Bu)P(H)N(*t*-Bu)].

The dihalodiphosphine 2,4-dichloro-1,3-di-*tert*-butyldiazadiphosphetidine, ClPN(*t*-Bu)P(Cl)N(*t*-Bu) (**1**), has recently been observed to undergo heterolytic P–Cl bond cleavage reactions promoted by $AlCl_3$[1,2] and NaCp*Mo-$(CO)_3$.[3,4] In the former case, a monocationic salt [ClPN(*t*-Bu)PN(*t*-Bu)$^+$][$AlCl_4^-$] (**2**) was reported. In the latter combination a monometallic complex,[5] Cp*Mo-$(CO)_2$[PN(*t*-Bu)P(Cl)N(*t*-Bu)] (**3**), and a bimetallic complex,[4] [Cp*Mo$(CO)_2]_2$[PN(*t*-Bu)PN(*t*-Bu)] (**4**), were isolated in high yield, and the structure of **4** was determined by single-crystal X-ray diffraction methods. The P_2N_2-$(t\text{-Bu})_2$ ring in **4** is planar, and a Cp*Mo$(CO)_2$ fragment is bonded to each phosphorus atom with the Mo atoms residing in the P_2N_2 plane. The Mo–P bond distance 2.246 (1) Å is short, and the average P–N bond distance 1.716 (3) Å is long compared to the distance found in **1**, 1.689 (4) Å.[6] On the basis of this structure we suggested that there exist formal Mo═P multiple bond interactions comprised of P lone pair → Mo dz^2 donation and Mo d_{xz} → p π^* back-donation.[7] The ligand **1** has subsequently revealed new, more complex chemistry with several other transition-metal fragments.[8] We report here on the interaction of $Na_2Fe(CO)_4\cdot{}^3/_2$dioxane[9] with **1** in a 1:2 ratio

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(3) Abbreviations used in the text include Cp* = $(CH_3)_5C_5$, THF = tetrahydrofuran, and Et_2O = diethyl ether.

(4) DuBois, D. A.; Duesler, E. N.; Paine, R. T. *Organometallics* **1983**, *2*, 1903.

(5) The monometallic complex **3** and the corresponding complex containing a C_5H_5 ligand in place of the Cp* ligand have been prepared and will be described in a subsequent paper. Light, R. W. Ph.D. Thesis, University of New Mexico, 1979.

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(7) The nature of the bonding interactions is closely related to that previously described for Cp*Mo$(CO)_2$ $PN(CH_3)CH_2CH_2NCH_3$: Hutchins, L. D.; Campana, C. F.; Paine, R. T. *J. Am. Chem. Soc.* **1980**, *102*, 4521.

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(9) Commercially available from Alpha Products, Thiokol, Ventron Division.

and on the crystal structure determination of the primary product isolated from the reaction.

The $Na_2Fe(CO)_4{\cdot}{}^3/_2$dioxane and diphosphine **1** were combined in vacuo in a 1:2 ratio in Et_2O or THF and stirred for 12 h at 25 °C.[10] No CO was evolved, and NaCl was filtered from the reaction mixture under dry nitrogen. Yellow crystals of **5** were obtained from an Et_2O solution cooled to 0 °C. Single-crystal X-ray diffraction analysis of **5** revealed its correct composition, $Fe_2(CO)_8\,[\overline{P(H)N(t\text{-}Bu)P(H)N}(t\text{-}Bu)]$. A view of the molecular structure is shown in Figure 1. The molecule contains the previously unreported cyclic diphosphine $H\overline{PN(t\text{-}Bu)P(H)N}(t\text{-}Bu)$ bonded to two $Fe(CO)_4$ fragments. The molecule possesses a center of symmetry with a trans arrangement of the $Fe(CO)_4$ groups. The nitrogen atom geometry is trigonal planar (sum of angles = 357.6°), the phosphorus atom geometry is tetrahedral, and the phosphorus atoms occupy *equatorial* coordination positions on the $Fe(CO)_4$ fragments. The last feature is quite unique since strong π-accepting ligands in most $Fe(CO)_4{\cdot}PX_3$ complexes occupy an axial coordination position.[11] The Fe–P bond distance, 2.178 (1) Å, compares favorably with the Fe–P distance in the neutral, axially substituted fluorophosphine complex,[12] $(CO)_4Fe\overline{P(F)N(CH_3)CH_2CH_2N}CH_3$ (**6**), 2.174 (7) Å; however, it is short compared to the range of distances typically found in many other axially substituted $Fe(CO)_4$·phosphine complexes, 2.237–2.364 Å.[11,13] It is interesting to note that the Fe–P distance in **5** is long compared to the average Fe–P distance in the *equatorially* substituted $Fe(CO)_4{\cdot}L^+$ phosphenium ion complex[14] $[(CO)_4FeP(NEt_2)_2{}^+]\,[AlCl_4{}^-]$ (**7**), 2.102 Å. The Fe–P bond shortening found in **7** is consistent with improved π-acceptor properties for the phosphenium ion ligand. The P–N bond distances in **5**, 1.702 (2) and 1.709 (2) Å, are longer than the P–N distance in **1**, 1.689 (4) Å, yet slightly shorter than the average distance in the bimetallic phosphenium ion complex **4**, 1.716 (3) Å. The P–N bond lengthening in **5** compared with **1** suggests a significant degree of $Fe \rightarrow (P_2N_2)$ ring back-bonding in this complex.

The $Fe(CO)_4{\cdot}L$ units in **5** adopt a distorted trigonal-bypyramidal geometry. The axial and equatorial Fe–CO bond distances (Å) are nearly equivalent: Fe(1)–C(2) = 1.784 (2), Fe(1)–C(3) = 1.792 (2) and Fe(1)–C(1) = 1.796 (3), and Fe(1)–C(4) = 1.793 (3), respectively. The P(1), Fe(1), C(1), and C(4) atoms form a plane with intraplanar angles P(1)–Fe(1)–C(4) = 132.1 (1)°, P(1)–Fe(1)–C(1) = 115.6 (1)°, and C(1)–Fe(1)–C(4) = 112.3 (1)°. The C(2) and C(3) atoms are distorted slightly toward the phosphine ligand as evidenced by the angles C(2)–Fe(1)–C(3) = 168.7 (1)°, P(1)–Fe(1)–C(2) = 85.0 (1)°, and P(1)–Fe(1)–C(3) = 86.1 (1)°. Other angles involving the carbonyl ligands include C(1)–Fe(1)–C(2) 94.7 (1)°, C(1)–Fe(1)–C(3) = 95.3 (1)°, C(2)–Fe(1)–C(4) = 90.0 (1)°, and C(3)–Fe(1)–C(4) = 90.8 (1)°. The Fe–C–O angles appear in a range 178.2 (2)° to 179.0 (2)°, and the C–O bond distances are found between 1.136 (3) and 1.142 (3) Å.

The solution infrared spectrum (isooctane) of **5** shows four absorptions: 1987 (s), 1972 (s), 1951 (vs), and 1948 (m) cm^{-1}. A $Fe(CO)_4{\cdot}L$ fragment with C_{3v} symmetry should show three carbonyl stretches (2a + e) while a fragment with C_{2v} symmetry should show four carbonyl bands (2a$_1$ + b$_1$ + b$_2$). Problems associated with distinguishing one $Fe(CO)_4{\cdot}L$ solution state structure from the other have been discussed in general by Darensbourg[15] and specifically for (aminophosphine)iron tetracarbonyl fragments by Cowley[16] and Parry.[17] On the basis of these analyses, the spectrum for **5** listed above may be interpreted in favor of an equatorial (C_{2v}) $Fe(CO)_4{\cdot}L$ structure. The $^{31}P\{^1H\}$ spectrum of **5** (THF) displays a singlet at 155.8 ppm (H_3PO_4 reference). Restoration of the proton coupling results in a doublet with $J_{PH} = 364.9$ Hz. These data are also consistent with the X-ray crystallographic analysis.

The source of the hydrogen atoms bonded to the phosphorus atoms has not yet been determined. Several potential hydrogen sources are available through degradation of solvents and stabilizers (diethyl ether, tetrahydrofuran, and dioxane), traces of water, or $NaHFe(CO)_4$ impurity in $Na_2Fe(CO)_4{\cdot}{}^3/_2$dioxane. Diethyl ether and THF seem to be eliminated since **5** is obtained in either solvent in approximately the same yields, and further studies are in progress that should distinguish between the remaining selections. Other studies indicate that the course of the reaction between **1** and $Na_2Fe(CO)_4$ is very sensitive to reaction conditions and reactant stoichiometry. Although the studies are incomplete, it appears that **5** is found in significant amounts only in the presence of excess ligand. Products isolated from the red fraction obtained here[10] and additional products formed with different reaction stoichiometries are under examination at this time.

Acknowledgment. R.T.P. wishes to acknowledge 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 78-2921, CHE 80-07979, and CHE 81-10536 which facilitated the purchases of the X-ray diffractometer, FT-IR spectrometer, and mass spectrometer. We also thank Dr. D. Wrobleski for several NMR spectra obtained at Los Alamos National Laboratory.

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(10) In a typical synthesis 0.500 g (1.45 mmol) of $Na_2Fe(CO)_4{\cdot}{}^3/_2$dioxane and a stir bar were added in a drybox to a 100-mL single-neck Schlenk vessel and 40 mL of dry diethyl ether was vacuum transferred onto the solid. Similarly, 0.400 g (2.90 mmol) of diphosphine **1** was loaded in a drybox into a separate 100-mL Schlenk vessel, and 30 mL of dry diethyl ether was vacuum transferred onto the solid. The two flasks were warmed to 25 °C, joined at their respective Teflon stopcock closures through a glass tee-connector (Solv-Seal joints), and the connecting space was evacuated. The contents of the flask containing the $Na_2Fe(CO)_4$ were stirred, and the solution of **1** was slowly dripped, over 30 min, into the $Na_2Fe(CO)_4$ solution. A color change, light yellow to deep red-yellow, was observed within 2 h, and the solution was stirred for a total of 12 h. No CO was evolved (Toepler pump), and NaCl was filtered from the red solution under dry nitrogen. The ether was vacuum evaporated, the residue extracted with dry benzene, and the resulting yellow solution filtered from a benzene-insoluble red solid. The benzene solution was vacuum evaporated, the residue redissolved in diethyl ether, and crystalline **5** obtained from a saturated diethyl ether solution held at 0 °C. Recrystallized **5** was obtained in 33% yield; mp 158–160 °C. Anal. Calcd for $Fe_2P_2O_8N_2C_{16}H_{20}$: C, 35.45; N, 5.16; H, 3.71. Found: C, 36.11; N, 4.81; C, 3.66. The product is air and moisture sensitive. The red residue that remains after the benzene extraction is soluble in THF and acetone. The residue contains at least two products as evidenced by infrared and NMR spectra, and these are difficult to completely separate from **5**. Full characterization of these products is in progress.

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(15) Darensbourg, D. J.; Nelson, H. H.; Hyde, C. L. *Inorg. Chem.* **1974**, *13*, 2135.

(16) Cowley, A. H.; Kemp, R. A.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 4289.

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

An Example of an "Inverted" Tetrahedral Geometry at Sulfur. The Synthesis and Crystal and Molecular Structure of $[HPtOs_3(CO)_8(\mu_4\text{-}S)(\mu_3\text{-}S)(PPh_2C_6H_4)]_2$

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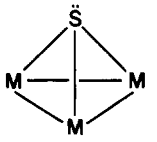
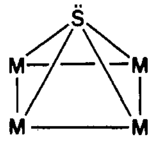
Summary: The decarbonylation of the sulfido-bridged cluster $PtOs_3(CO)_{10}(PPh_3)(\mu_3\text{-}S)_2$, **1**, by trimethylamine oxide leads to formation of the dimer $[HPtOs_3(CO)_8(\mu_4\text{-}S)(\mu_3\text{-}S)(PPh_2C_6H_4)]_2$, **2**. The molecular structure of **2** was determined by single-crystal X-ray diffraction analysis: space group $P2_1/n$, $a = 14.308$ (2) Å, $b = 21.753$ (5) Å, $c = 21.760$ (4) Å, $\beta = 96.20$ (1)°, $Z = 4$, $\rho_{calcd} = 2.83$ g/cm^3. The structure was solved by a combination of direct methods and difference Fourier techniques and was refined with 4874 reflections to the final residuals of $R_F = 0.053$ and $R_{wF} = 0.063$. Compound **2** consists of two trigonal-prismatic $PtOs_3S_2$ clusters linked on an edge by quadruply bridging sulfido ligands that serve as six-electron donors and exhibit inverted tetrahedral geometries.

Bridging ligands have been shown to be of great value for the synthesis and stabilization of transition-metal cluster compounds.[2-4] Of these the sulfido ligand has been the focus of considerable attention.[5-8] Triply bridging sulfido ligands A serve as four-electron donors while quadruply bridging sulfido ligands can serve either as four B or six C electron donors.[3] The type C geometry is best described as tetrahedral, although the M–S–M bond angles often span wide ranges due to distortions caused by the existence of metal–metal bonding.[3,9] We now wish to report the characterization of a complex containing quadruply bridging sulfido ligands that are so greatly distorted that their geometry should be described as "inverted" tetrahedral.[10,11]



A



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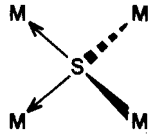

C

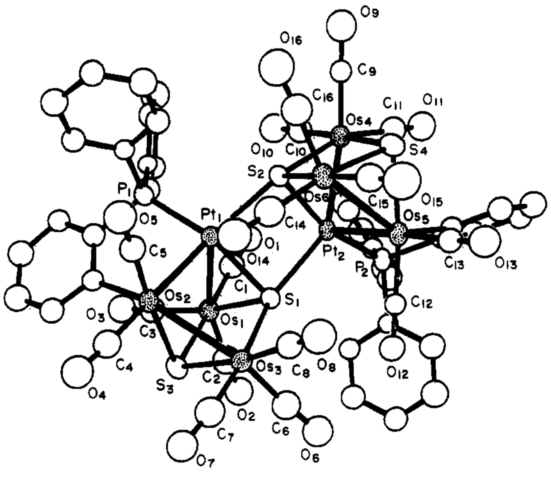

Figure 1. An ORTEP diagram of $[HPtOs_3(CO)_8(\mu_4\text{-}S)(\mu_3\text{-}S)(PPh_2C_6H_4)]_2$, **2**, showing 50% probability thermal ellipsoids.

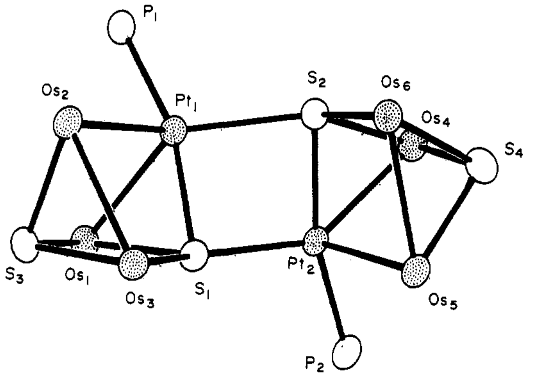

Figure 2. An ORTEP diagram of **2** with the phenyl rings and carbonyl ligands omitted.

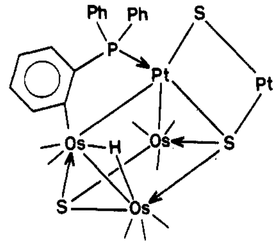

Figure 3. An electron distribution scheme showing the bonding for one half of the molecule of **2**.

Treatment of the complex $PtOs_3(CO)_{10}PPh_3(\mu_3\text{-}S)_2$, **1**,[12] with trimethylamine oxide dihydrate in THF at 0 °C for 1 h results in the formation of the orange-red product $[HPtOs_3(CO)_8(\mu_4\text{-}S)(\mu_3\text{-}S)(PPh_2C_6H_4)]_2$, **2**, in 16% yield.[13] The structure of **2** was determined by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of the complete molecule is shown in Figure 1.[14] An ORTEP diagram

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(13) The reaction was performed at 0 °C over a period of 1 h. The orange product **2** was isolated by TLC on silica by using a hexane/methylene chloride solvent mixture: IR (ν(CO), cm^{-1}, in hexane) 2104 (m), 2099 (s), 2079 (s), 2073 (m), 2031 (s), 2016 (m), 2006 (s), 2003 (s), 1989 (m), 1947 (s); ^{1}H NMR (δ, $CDCl_3$) 6.70–8.00 (m, 28 H), −11.17 (d, 2 H, $J_{P\text{-}H} = 9.6$ Hz).

(14) Compound **2** crystallizes in the monoclinic space group $P2_1/n$: $a = 14.308$ (2) Å, $b = 21.753$ (5) Å, $c = 21.760$ (4) Å, $\beta = 96.20$ (1)°, $V = 6733$ (4) Å^3, $Z = 4$, $\rho_{calcd} = 2.83$ g/cm^3. Intensity data were collected on an Enraf-Nonius CAD4 X-ray diffractometer by using Mo K$_{\bar{\alpha}}$ radiation. The structure was solved by a combination of direct methods (MULTAN) and difference Fourier techniques. Full-matrix least-squares refinement (4874 reflections, $F^2 \geq 3.0\ \sigma(F^2)$) yielded the final residuals $R_F = 0.053$ and $R_{wF} = 0.063$. All calculations were performed on a Digital Equipment Corp. VAX 11/750 using the Enraf-Nonius SDP program library.

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