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Synthesis and Structure of a Bimetallic Diphosphenium Ion Complex Containing a Diazadiphosphetidine Ring

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Summary: The reaction of NaMo[η⁵-(CH₃)₅C₅](CO)₃ with CIPN(*t*-Bu)P(Cl)N(*t*-Bu) in a 2:1 ratio in THF results in the formation of a metallophosphenium ion complex Mo₂-[(CH₃)₅C₅]₂(CO)₄[PN(*t*-Bu)PN(*t*-Bu)]. The compound has been characterized by IR and ¹H, ¹³C, and ³¹P NMR spectroscopy, and the structure has been determined by X-ray diffraction techniques. The neutral molecular complex can be considered to be derived from the union of the phosphorus atoms on a formal dicationic diazadiphosphetidine ring [PN(*t*-Bu)PN(*t*-Bu)²⁺] with the Mo atoms from two Mo[η⁵-(CH₃)₅C₅](CO)₂⁻ fragments.

Heterolytic cleavage of phosphorus-halogen bonds in selected uncoordinated and metal-coordinated aminohalophosphines is promoted with classical halide acceptors and metal carbonylate nucleophiles. By utilizing this procedure, dicoordinate aminophosphenium ions¹ [(R₂N)(X)P⁺], cationic metallophosphenium ion complexes² M(CO)_x[(R₂N)(X)P]⁺, and neutral metallophosphenium ion complexes³ M(CO)_y[(R₂N)(X)P] have recently been prepared. The majority of the compounds have been obtained from monophosphine ligands, and only a few attempts to prepare phosphenium ions from diphosphine precursors have been described. In particular,

Scherer⁴ observed that the combination of AlCl₃ and the diazadiphosphetidine CH₃PN(*t*-Bu)P(Cl)N(*t*-Bu) results in the formation of a monophosphenium ion CH₃PN(*t*-Bu)PN(*t*-Bu)⁺ (1), while Keat⁵ noted the formation of a related monocation [Me₂NPN(*t*-Bu)PN(*t*-Bu)⁺] (2). Cowley and co-workers^{1h} have investigated similar chemistry of 2,4-dichloro-1,3-di-*tert*-butyldiazadiphosphetidine, and even in the presence of excess AlCl₃ only the monocation [CIPN(*t*-Bu)PN(*t*-Bu)⁺] (3) was found. No evidence for the formation of a dication [PN(*t*-Bu)PN(*t*-Bu)²⁺] (4) was reported. Diazadiphosphetidine ligands should provide a convenient template for the construction of a number of unusual metallophosphenium ion complexes,⁶ and the rich chemistry of XPN(*t*-Bu)P(X)N(*t*-Bu) ligands with metal carbonylate reagents have been examined in our laboratory.⁷ We report here the synthesis and molecular structure determination for the first bimetallic diphosphenium ion complex that can be considered to contain the dication 4.

Combination of CIPN(*t*-Bu)P(Cl)N(*t*-Bu)⁸ (5) with 2 equiv of NaMo[η⁵-(CH₃)₅C₅](CO)₃⁹ in tetrahydrofuran (THF) results in the evolution of 90% of 2 equiv of CO, precipitation of NaCl, and the formation of a red-orange air-sensitive solid, 6.^{10,11} These observations and the spectroscopic and structural data described below are consistent with eq 1.

The infrared spectrum of 6 in cyclohexane shows two strong carbonyl bands at 2014 and 1931 cm⁻¹ which is consistent with the presence of two terminal carbonyls on each molybdenum atom. The positions of these bands are similar to those reported for Mo[(CH₃)₅C₅](CO)₂NO (2015 and 1935 cm⁻¹)¹² and higher in frequency than the bands found in Mo[(CH₃)₅C₅](CO)₂[PN(CH₃)CH₂CH₂NCH₃] (1902 and 1810 cm⁻¹).¹³ This suggests that the diphosphenium ion 4 displays π-acceptor ability similar to

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(10) Compound 6 was isolated under inert-atmosphere conditions. The THF solution was filtered, and the filtrate was vacuum evaporated. The resulting solid was extracted with benzene and recovered in 85% yield by vacuum evaporation of the benzene. Carbon monoxide was recovered in 90% yield from the original reaction mixture by using a Toepfer pump: infrared spectrum (carbonyl region, cyclohexane) 2014 (s), 1931 cm⁻¹; ¹H NMR (benzene, Me₄Si standard) δ 1.65 (m, *t*-Bu methyl), 2.24 (s, Cp* methyl); ¹³C{¹H} NMR (Me₄Si standard) δ 103.25 (s, Cp* ring), 31.59 (m, *t*-Bu methyl) 11.37 (d, ³J_{CP} = 2.5 Hz Cp* methyl); ³¹P{¹H} NMR (85% H₃PO₄ standard) δ 224.65 (s).

(11) The monometallic complexes Mo(CO)₂[η⁵-(CH₃)₅C₅]PN(*t*-Bu)P(Cl)N(*t*-Bu) and Mo(CO)₂(η⁵-C₅H₅)PN(*t*-Bu)P(Cl)N(*t*-Bu) have also been prepared and fully characterized. These complexes will be described in full along with 4 in a future paper: Dubois, D. A.; Light, R. W.; Duesler, E. N.; Paine, R. T., to be submitted for publication.

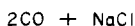
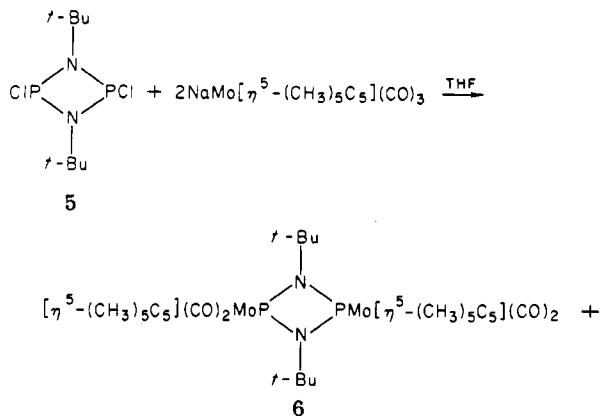
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that of the nitrosyl ligand and much greater than that of the cyclic monophosphenium ion $[\text{PN}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NCH}_3]^+$. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra¹⁰ display resonances that can be confidently assigned to the Cp^* ring¹⁴ and the N - t -Bu groups of the ligand. In the past, the formation of phosphonium ions and metallophosphenium ion complexes has been accompanied by a large downfield shift of the ^{31}P NMR resonance for the cationic ligand compared to its neutral precursor.¹⁻³ The $^{31}\text{P}\{^1\text{H}\}$ spectrum of 6, on the other hand, shows a single resonance at 224.6 ppm that is only slightly downfield of the resonance in $\text{CIPN}(t\text{-Bu})\text{P}(\text{Cl})\text{N}(t\text{-Bu})$, 206 ppm. The resonance in 6 is considerably upfield of resonances assigned to cationic phosphorus atoms in the monophosphenium ions 1-3, several monometallic phosphonium ion complexes containing 3,^{2,3,15} and the metal complexes of several other phosphonium ions.¹⁵ The small coordination shift found in 6 might be initially interpreted to indicate the formation of a simple phosphine \rightarrow organomolybdenum coordination complex from the neutral diazadiphosphetidine ligand, $\text{CIPN}(t\text{-Bu})\text{P}(\text{Cl})\text{N}(t\text{-Bu})$. On the other hand, factors that contribute to low-field shifts for most phosphonium ions and their metal complexes are not well understood. Speculation over the small shift in 6 is not appropriate until a theoretical evaluation of ^{31}P shifts in phosphonium ions and additional data for related bimetallic complexes become available.¹⁶

An X-ray crystal structure determination confirms the proposed composition of 6. A view of the molecular structure is shown in Figure 1. The molecule contains a center of inversion, and the P_2N_2 ring is planar with the Mo atoms 0.055 Å above and below the plane. Each Mo atom is bonded to a planar Cp^* ring in an η^5 -fashion with $\text{Mo}-\text{C}(\text{ring})_{\text{av}} = 2.373$ (4) Å, $\text{C}(\text{ring})-\text{C}(\text{ring}) = 1.418$ (5) Å, and $\text{C}(\text{ring})-\text{CH}_3 = 1.507$ (5) Å. These distances are

(14) Abbreviations used in the text include: $\text{Cp}^* = [\eta^5\text{-(CH}_3)_5\text{C}_5]$, $\text{Cp} = (\text{C}_5\text{H}_5)$, and THF = tetrahydrofuran.

(15) Phosphorus-31 NMR data δ (ppm): 1, 252;⁴ 2, 331.5;⁵ 3, 363;^{1h} $\text{MoCp}(\text{CO})_2\text{PN}(t\text{-Bu})\text{P}(\text{Cl})\text{N}(t\text{-Bu})$, 275.6, 184.6;⁷ $\text{MoCp}^*(\text{CO})_2\text{PN}(t\text{-Bu})\text{P}(\text{Cl})\text{N}(t\text{-Bu})$, 258.2, 181.5; $\text{MoCp}(\text{CO})_2\text{PN}(t\text{-Bu})\text{P}(\text{F})\text{N}(t\text{-Bu})$, 277.3, 277.3, 161.3; $\text{MoCp}(\text{CO})_2[\text{PN}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NCH}_3]$ 271.6.^{3c}

(16) Previous discussions of ^{31}P NMR shifts for phosphonium ions have assumed that diamagnetic contributions dominate these shifts. Fenske and co-workers have noticed that low-field ^{13}C shifts in some carbene complexes appear to have significant paramagnetic contributions, and attempts to theoretically model these shifts have been presented. Similar paramagnetic contributions to ^{31}P shifts may appear in metallophosphenium ion complexes; therefore, great care must be used in deducing the nature of these complexes from ^{31}P NMR data alone. Fenske, R. F. National Meeting of the 184th American Chemical Society, 1982 New York, Aug 1982; American Chemical Society: Washington, DC, INOR 1.

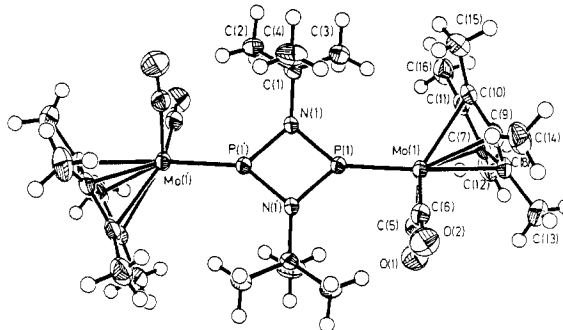


Figure 1. Molecular geometry and atom labeling scheme for $\text{Mo}_2[\eta^5\text{-(CH}_3)_5\text{C}_5]_2(\text{CO})_4[\text{PN}(t\text{-Bu})\text{PN}(t\text{-Bu})]$.

similar to those found in $\text{MoCp}^*(\text{CO})_2[\text{PN}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NCH}_3]$ ¹³ (7): $\text{Mo}-\text{C}(\text{ring}) = 2.360$ (15) Å, $\text{C}(\text{ring})-\text{C}(\text{ring}) = 1.406$ (10) Å, and $\text{C}(\text{ring})-\text{CH}_3 = 1.511$ (5) Å. Each Mo atom is also bonded to two terminal carbonyls with $\text{Mo}-\text{CO}_{\text{av}} = 1.942$ (4) Å, $\text{C}\equiv\text{O} = 1.159$ (5) Å, and $\text{C}(5)-\text{Mo}-\text{C}(6) = 87.8$ (2)°. These parameters also can be compared to parameters in 7: $\text{Mo}-\text{CO} = 1.945$ (14) Å, $\text{C}\equiv\text{O} = 1.152$ (6) Å, and $\text{C}-\text{Mo}-\text{C} = 85.3$ (2)°. The $\text{Mo}(\text{CO})_2$ plane is approximately perpendicular to the P_2N_2 plane (87.7° interplanar angle). The $\text{Mo}-\text{P}$ distance in 6, 2.246 (1) Å, is slightly longer than the $\text{Mo}-\text{P}$ distances in the phosphonium ion complexes $\text{MoCp}(\text{CO})_2\text{PN}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NCH}_3$, 2.213 (1) Å, and 7, 2.217 (1) Å, yet it is considerably shorter than the normal range of distances, 2.33-2.58 Å, found in most organomolybdenum-phosphine complexes.¹⁷ The average $\text{P}-\text{N}$ bond distance, 1.716 (3) Å, in 6 is longer than the $\text{P}-\text{N}$ bond distance in 5, 1.689 (4) Å,¹⁸ and the $\text{N}-\text{P}-\text{N}'$ and $\text{P}-\text{N}-\text{P}'$ bond angles, 81.7 (1) and 98.3 (1)°, are respectively slightly smaller and larger than the corresponding angles in 5. Finally, the sums of the angles about the phosphorus and nitrogen atoms are 360 and 356.5°. The planar geometry about the phosphorus atom in 6 with a $\text{Mo}-\text{P}-\text{N}$ angle of 142.8 (1)° contrasts with the tetrahedral geometry about phosphorus in the precursor ligand 5 with a $\text{Cl}-\text{P}-\text{N}$ angle 103.3°.

The composition, planarity of the P_2N_2 ring, the short $\text{Mo}-\text{P}$ bond distance, and the elongated $\text{P}-\text{N}$ bond distances are consistent with the classification of 6 as a neutral, molecular metallophosphenium ion complex conceptually constructed from the combination of two 16-electron $\text{MoCp}^*(\text{CO})_2^-$ fragments and a dicationic diphosphenium ion 4. The bonding in 6 should be qualitatively related to that described previously for $\text{MoCp}(\text{CO})_2[\text{PN}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NCH}_3]$.^{3,13} The dication 4 has an in-plane lone pair localized on each phosphorus atom which can be donated into empty d_{z^2} orbitals on the two $\text{MoCp}^*(\text{CO})_2^-$ fragments, and this overlap provides $\text{P} \rightarrow \text{Mo}$ σ interactions. In addition, each metal fragment has an occupied d_{xz} orbital that can donate electron density into a degenerate, empty π^* MO on the dication. This overlap furnishes efficient $\text{Mo} \rightarrow \text{P}$ π back-donation. Together, these interactions would provide the observed short $\text{Mo}-\text{P}$ and elongated $\text{P}-\text{N}$ distances found in 6. Additional novel coordination chemistry of 3 and 4 with $\text{CpFe}(\text{CO})_2^-$, $\text{Mn}(\text{CO})_5^-$, and $\text{Fe}(\text{CO})_4^{2-}$ fragments will be described shortly.

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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.

Stepwise Reduction of Carbon Disulfide in the Coordination Sphere of Tungsten. A Transition-Metal-Mediated Synthesis of Dithioacetals¹

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Summary: Reduction of *mer*-W(CO)₃(dppe)(η²-CS₂) (1) with LiHBEt₃ yields the dithioformate complex *fac*-Et₄N⁺[W(CO)₃(dppe)(η¹-SCHS)]⁻ (2) which may also be obtained by a simple ligand exchange reaction. Compound 2 reacts with alkyl halides in two steps via dithio ester complexes *mer*-W(CO)₃(dppe)(η²-SCHSR) (3) to dithiocarbenium ion derivatives *mer*-[W(CO)₃(dppe)(η²-R'SCHSR)]X (4). LiHBEt₃ reduces 4 to dithioacetal complexes *mer*-W(CO)₃(dppe)(η¹-R'SCH₂SR) (5) which isomerize photochemically to the corresponding *fac* compounds 6. Lewis bases readily displace the dithioacetal from 6 but not from 5.

Transition-metal complexes of carbon disulfide are often seen as models for analogous but less readily available complexes of carbon dioxide. Studies of their reactivity may ultimately help in the development of transition-metal-mediated conversions of CO₂ into organic products.

The number of known CS₂ complexes is vast,² and their reactions include electrophilic attack at sulfur,² sulfur abstraction,² cycloaddition with alkynes,³ coupling with CS₂,⁴ and oxidation to thiocarbonato species.⁵

After we had found that trialkylphosphines add at the CS₂ carbon atom of *mer*-W(CO)₃(dppe)(η²-CS₂) (1),^{3f} we looked for reactions of other simple nucleophiles with 1. Indeed, 1 reacts smoothly with Li[HBEt₃] to give *fac*-[W(CO)₃(dppe)(η¹-SCHS)]⁻ (2) which is isolated as Et₄N⁺ salt.⁶ Dithioformate complexes have mostly been obtained

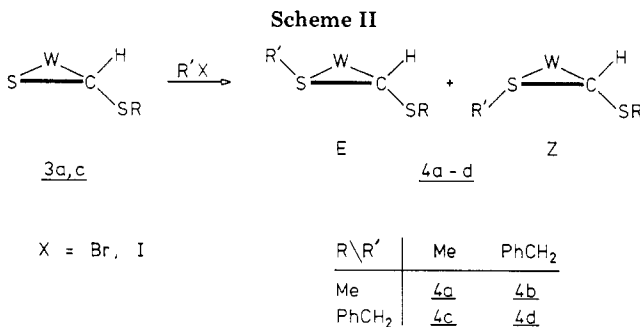
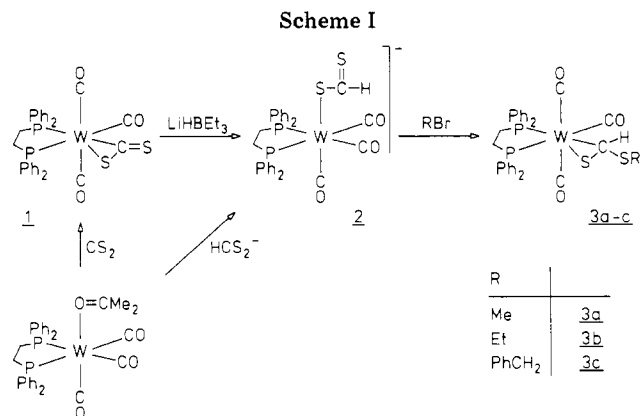
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by insertion of CS₂ into metal-hydrogen bonds.⁷ 2 and a number of other dithioformate complexes can also be prepared simply by ligand exchange reactions^{8,9} (Scheme I).

2 reacts readily with mild alkylating agents such as alkyl or benzyl halides. Thus reaction with a stoichiometric amount of methyl bromide gives the methyl dithioformate complex 3a.¹⁰ Similarly the ethyl and benzyl derivatives

(6) A solution of 1 (0.26 g, 0.35 mmol) in THF (30 mL) is treated with a slight excess of LiHBEt₃ (0.5 M in THF). After addition of Et₄NBr (0.3 g, 1.4 mmol, dissolved in 10 mL of CH₂Cl₂) the solution is taken to dryness and the residue recrystallized twice from CH₂Cl₂/ethanol to remove LiBr and some dark decomposition products. 2 is isolated as dark orange microcrystalline powder in 46% yield.

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(8) To a solution of W(CO)₃(dppe)(acetone), freshly prepared by photolyzing W(CO)₄(dppe) (5.52 g, 7.95 mmol) in acetone,^{3f} is added Et₄N[HCS₂] (2.07 g, 10.0 mmol). After evaporation to dryness, the residue is dissolved in 200 mL of CH₂Cl₂, some violet byproduct is filtered off, and ethanol (50 mL) is added. Upon slow evaporation in vacuo an orange powder separates. Recrystallization from CH₂Cl₂/ethanol yields 5.0 g (72%) of 2: IR ν(CO) (CH₂Cl₂) 1910 (s), 1815 (s), 1790 (s) cm⁻¹; ¹H NMR (CH₂Cl₂, 60 MHz) HCS₂, 11.4 ppm. Anal. Calcd for C₃₈H₄₅NO₃P₂S₂W: C, 52.24; H, 5.19; N, 1.60. Found: C, 52.39; H, 5.22; N, 1.57.

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(10) A solution of 2 (0.87 g, 1.0 mmol) in THF (50 mL) is treated with a stoichiometric amount of methyl bromide. After 1.5 h the solution is filtered through Celite and evaporated to 20 mL. Addition of 10 mL of ethanol and further evaporation give 3a (0.50 g, 66%) as orange powder: ¹H NMR (CDCl₃, 60 MHz) HCS₂, 5.30, SCH₃, 2.57 ppm. Anal. Calcd for C₃₁H₂₈O₃P₂S₂W: C, 49.09; H, 3.72. Found: C, 49.18; H, 3.83. 3b and 3c were prepared similarly. 3b: yield 55%; ¹H NMR (CDCl₃, 60 MHz) HCS₂, 5.23, SCH₂, 2.85, CH₃, 1.33 ppm (³J(H-H) = 7.5 Hz); ¹³C NMR (CDCl₃, 100 MHz) HCS₂, 47.63 (¹J(C-H) = 179 Hz), SCH₂, 37.27 (¹J(C-H) = 137 Hz), CH₃, 14.20 (¹J(C-H) = 126 Hz), CO(eq), 211.8, CO(ax), 198.8, 197.6 ppm; ³¹P NMR (CDCl₃, 36.44 MHz) 41.7 (¹J(W-P) = 209 Hz), 42.6 ppm (¹J(W-P) = 219 Hz, ²J(P-P) = 15 Hz). Anal. Calcd for C₃₂H₃₀O₃P₂S₂W: C, 49.75; H, 3.91; S, 8.30. Found: C, 49.98; H, 3.87; S, 8.38. 3c: yield 77%; ¹H NMR (CDCl₃, 60 MHz) HCS₂, 5.15; SCH₂, 4.10 ppm. Anal. Calcd for C₃₇H₃₂O₃P₂S₂W: C, 53.25; H, 3.86; S, 7.68. Found: C, 53.42; H, 4.09; S, 7.86.