with substrates such as sulfur dioxide (reversibly), hydrogen chloride, and methyl iodide, although unlike *trans*-IrCl(CO)$(PPh_3)_2$ it does not bind molecular oxygen.

Acknowledgment. This research was supported by Dow Chemical Co. FD and FAB mass spectra were obtained in the Mass Spectrometry Laboratory, which is supported by a grant from the National Institute of General Medical Sciences (GM 27029).

Registry No. *cis*-$PtCl_2[Cu(acacP)_2]$, 81141-51-7; *cis*-$PdCl_2[Cu(acacP)_2]$, 81141-52-8; $PtCl_2(HacacP)_2$, 81141-53-9; $PdCl_2(HacacP)_2$, 81141-54-0; $Ir(acacP)(CO)_2$, 81141-55-1; Ir(acacP)(COD), 81141-56-2; $[PtCu(acacP)_2](BF_4)_2$, 81141-58-4; $RuCl_2(HacacP)_2$, 81157-61-1; $RuCl_2[Cu(acacP)_2]$, 81141-59-5; *trans*-$IrCl(CO)(HacacP)_2$, 81157-62-2; *trans*-$IrCl(CO)[Cu(acacP)_2]$, 81141-60-8; $[IrCl(COD)]_2$, 12112-67-3; $PtCl_2(COD)$, 12080-32-9; $PdCl_2(COD)$, 12107-56-1; $RuCl_2(PPh_3)_3$, 15527-49-4; $IrCl(CO)_2(p\text{-}H_2NC_6H_4Me)$, 59952-74-8.

Supplementary Material Available: Tables of structure factors, positional parameters, thermal parameters, angles, distances, and a complete structural report for $Cl_2Pt[Cu(acacP)_2]$ (51 pages). Ordering information is given on any current masthead page.

Synthesis and Molecular Structure of a Transition-Metal Cyclamphosphoranide. A Pentacyclic Structure with the Metal Bridging a P-N Bond

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Received December 18, 1981

Cyclamphosphorane **1** and related compounds[1] have recently given rise to considerable interest. Their polycyclic structures engender original behavior: they have led to phosphonium ions that undergo a remarkable dimerization,[2] to the first P(V)-P(V) compound, dicyclendiphosphorane,[3] to the first phosphonium salts containing ionic fluoride,[4] under X-ray irradiation to a phosphoranyl radical[5] remarkably stereodynamic in the solid, etc. We now report the displacement of the tautomeric equilibrium **1** under the action of a transition-metal derivative and the easy formation of stable transition-metal phosphoranides.

The first transition-metal phosphoranides, i.e., compounds in which a 4-connected phosphoranide anion, **2**, acts as a donor ligand toward a transition metal, have recently been obtained from bicyclic aminophosphoranes.[6,7] The tetracyclic structure of **1** appears to convey additional stability to such phosphoranide adducts.

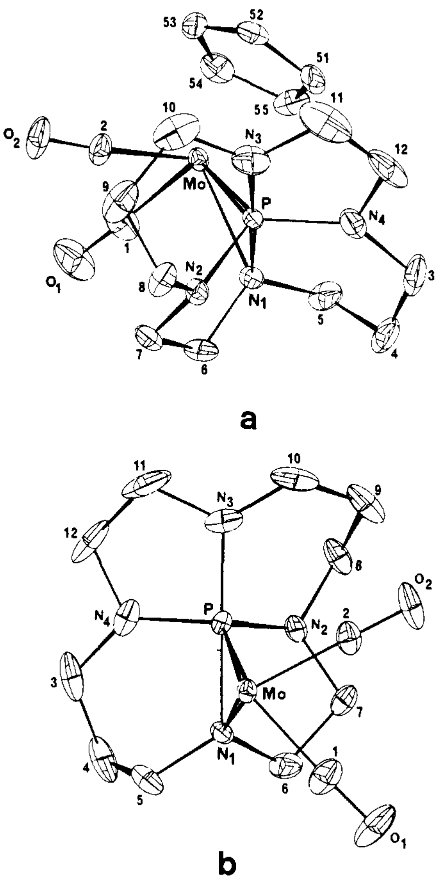

Figure 1. (a) ORTEP diagram showing the trigonal bipyramidal arrangement of the bonds on phosphorus. (b) View of the NMoP bridge and pentacyclic structure. The η^5-C_5H_5 ring has been omitted in **1b** for clarity. Selected bond lengths, Å (and standard deviations): P-Mo, 2.444 (2); P-N_1, 1.854 (5); P-N_2, 1.697 (6); P-N_3, 1.696 (7); P-N_4, 1.670 (7); N_1-Mo, 2.223 (5). Angles (°); $MoPN_1$, 60.5 (2); $MoPN_2$, 116.4 (2); $MoPN_3$, 116.2 (2); $MoPN_4$, 118.0 (2); N_1PN_3, 176.6 (3); N_2PN_4, 117.6 (3); N_1PN_4, 93.8 (3); N_1PN_2, 87.8 (3); N_2PN_3, 93.5 (3); N_3PN_4, 88.4 (4).

Solutions of cyclamphosphorane have been shown by Atkins and Richman to consist of an equilibrated mixture of the closed (**1a**) and open (**1b**) tautomers. When this mixture is allowed to react with $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$,[8] the equilibrium is quantitatively shifted to the right, with formation of a mixture of adducts **3** and **4**, in which the open cyclamphosphane form behaves either as a monodentate (through P) or a bidentate (through P and one N) *ligand* toward the transition metal. Compounds **3** and **4** are characterized[9] in the mixture by two signals in the ${}^{31}P$ NMR spectrum at 144.6 and 149.8 ppm, with respective peak areas of 25% and 75%.[10] Conductimetric measurements in acetone solutions are consistent with the presence of ca. 20% of an ionic species. Only the ionic constituent of the reaction mixture appears to undergo nucleophilic attack under the action of LiMe to give the phosphoranide **6**. Formulations **3** + **4** are further asserted by their quantitative conversion to **5** under the action of $NaBPh_4$. Compound **5** arises as two diastereoisomers (δ (${}^{31}P$) +144.8; δ (${}^{1}H_{Cp(1)}$) 5.60, δ (${}^{1}H_{Cp(2)}$) 5.73 in a 17:83 ratio).

The molybdenum cyclamphosphoranide **6** was obtained in over 90% yield when a THF solution of **5** was treated with 1 equiv of LiMe for 1 h at room temperature. It occurs as yellow-orange crystals, moderately air sensitive, soluble in THF and $CHCl_3$, and

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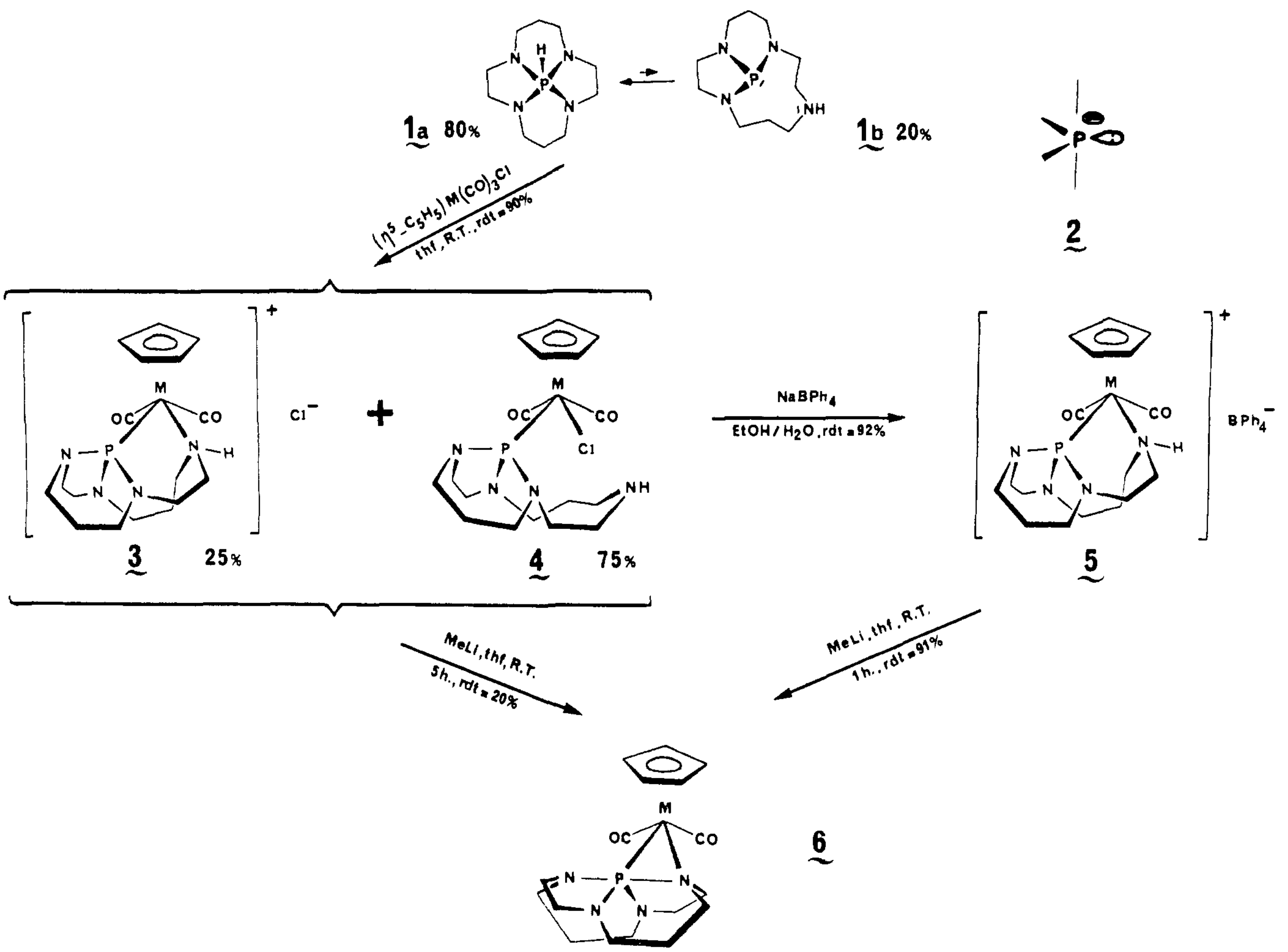
[10] The Cp ring exhibits four singlets in the ${}^{1}H$ NMR spectrum (5.54 (48%), 5.59 (22%), 5.79 (22%), 5.83 (7%) ppm), which is consistent with the possibility of having two diastereomers for both **3** and **4**.



slightly soluble in ether, pentane, and CH_2Cl_2. It appears to be indefinitely stable at room temperature under dry nitrogen or argon and decomposes without melting at around 150 °C.

All spectroscopic and analytical data are in accord with structure **6**: the δ ^{31}P peak is shifted from ca. 150 in compounds **3–5** to −31.0.[6,7] Only one signal was detected in both ^{31}P and ^1H (5.90 ppm) NMR spectra, indicating that only one of the two possible diastereomeric structures of **6** is formed (P, N, and M are asymetric but P and N not independently). The infrared spectra (KBr pellet) show the expected two ν(CO) vibrations at 1802 and 1906 cm^{-1}.

The structure of **6** was established definitely by X-ray diffraction. It forms monoclinic crystals with space group $P2_1/n$ and unit cell parameters $a = 13.736$ (1) Å, $b = 9.354$ (2) Å, $c = 15.577$ (2) Å, $\beta = 113.05$ (1)°, $V = 1841.65$ Å^3, $Z = 4$. The intensities of 5592 refractions ($2 < \theta < 30°$; Mo Kα radiation) were collected. No decrease in the intensity of three standard reflections recorded periodically was observed during the data collection. The data were corrected for Lorentz and polarization factors and for anomalous dispersion of the Mo atom, but not for absorption. The structure was solved by the heavy-atom method. Fourier synthesis allowed the location of all nonhydrogen atoms. A preliminary refinement was made on 2315 reflections to reach R_w and R values of 0.044 and 0.068, respectively. At this stage of refinement a Fourier difference map showed the hydrogen atoms. They were introduced isotropically but not refined. The final R_w and R factors reached values of 0.034 and 0.067.

The structure (Figure 1) shows many remarkable features, e.g., the 5-connected character, i.e., phosphoranide behavior, of the phosphorus atom, and its belonging, for the first time to our knowledge, to five cycles at a time (the only two transition-metal phosphoranides reported so far derive from bicyclic phosphoranes and have a tricyclic structure). In spite of this, the arrangement of the five bonds around phosphorus is surprisingly close to a regular trigonal bipyramid. Thus the N_1, P, and N_3 atoms are almost aligned (176 ± 0.9°), and the angles in the equatorial plane are all close to 120° (118.0 ± 0.6; 116.4 ± 0.6; 117.6 ± 0.9°). The Mo–P bond (2.44 Å) is short when compared to those of analogous molybdenum(II) phosphane adducts (2.45–2.52 Å),[11] as expected for equatorial bonds in a trigonal-bipyramidal structure. The unusual bridging of the P–N bond by a transition metal is certainly related to the very long P–N bond (1.85 Å) (and absence of any significant $p_{N\pi}$–$d_{P\pi}$ interaction) and results in a normal (2.22 Å) Mo–N bond. Also unique is the observation that *all* the uncoordinated nitrogen atoms (including the *apical* one, which usually has a very distinct character[12]) present short N–P bonds (1.697, 1.696, and 1.670 Å with respectively N_2, N_3, and N_4) and nearly coplanar arrangements with their substituents (sum of the angles, 350 ± 1.5, 357.0 ± 2.1, and 360 ± 2.1° about N_2, N_3, and N_4, respectively). The unusual length of the P–N_1 bond may cause a certain amount of the $p_{N\pi}$–$d_{P\pi}$ interaction to be transferred into the P–N_3 bond in the trans structure, with the result that it is not the apical N_3 but the equatorial N_2 atom that departs most from planarity.

Similar behavior was observed when the tungsten analogue of salt **5** was treated with LiMe. The corresponding cyclamphosphoranide was isolated in 93% yield as orange-yellow crystals (δ (^{31}P) −52, $^1J_{P-^{183}W} = 250$ Hz) that exhibit the expected analytical and spectral characteristics.

Acknowledgment. We thank Drs. D. U. Robert and B. Septe for measuring the mass spectra and NMR spectra, respectively, and the donors of the Petroleum Research Fund, administered

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by the American Chemical Society, for partial support of this work.

Registry No. 1a, 64317-99-3; **1b**, 64318-00-9; **3**, 81121-00-8; **4**, 81121-01-9; **5** (M = Mo), 81121-03-1; **5** (M = W), 81121-05-3; **6** (M = Mo), 81120-90-3; **6** (M = W), 81120-91-4; (η^5-C_5H_5)Mo(CO)$_3$Cl, 12128-23-3.

Supplementary Material Available: Listings of atomic positions, thermal parameters, bond lengths, and bond angles (2 pages). Ordering information is given on any current masthead page.

Dithiaethylene Radical Cations and Anions[1]

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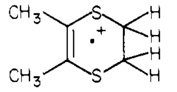
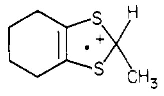
Received November 6, 1981

Hyperfine splittings (hfs) by hydrogen atoms α to a sulfur atom with unpaired spin density in the ESR spectra of tetrathiaethylene ($(RS)_2C{=}C(SR)_2$) radical cations have been interpreted[2,3] as arising mainly or solely from an angle-independent spin polarization ($|a_\alpha{}^H| = 17\rho_S$ G),[3] in contrast to the hyperconjugation mechanism that dominates for carbon-centered radicals.[4] We have tested this interpretation by comparing systems with one and two sulfur atoms with unpaired electron spin density attached to a carbon atom bearing a proton, e.g., **1** and **2**. A spin polarization mechanism with $Q^{\cdot}{}_{SCH}{}^H = 17$ requires $\rho_S(\mathbf{1}) = 0.27$ and $\rho_S(\mathbf{2})$ to have the impossible value of 0.71 ($\rho_S(\mathbf{2}) = 24.2/2\ (17)$). The high value of $a_\alpha{}^H$ for the methine hydrogen of **2** requires a delocalization mechanism. The unpaired electron in the π system is in a symmetric SOMO, which leads to the hyperconjugation predictions;[5] $a_\alpha{}^H(1) = B(c_S)^2\ \langle\cos^2\theta\ (\mathbf{1})\rangle$ and $a_\alpha{}^H(2) = B(2c_S)^2\langle\cos^2\theta\ (\mathbf{2})\rangle$, where c_S is the MO coefficient for the S atom in the SOMO and θs are the dihedral angles between the C–H bonds and the sulfur p orbitals with unpaired electron spin. Utilizing the value of B for $CH_3\dot{S}O$ of 25.4 G[4c] and $a_{\dot{C}CH_3}{}^H = 27\rho_C$ leads to $\rho_S = c_S{}^2 = 0.29$, $\langle\cos^2\theta\ (\mathbf{1})\rangle = 0.5$, $\langle\cos^2\theta\ (\mathbf{2})\rangle = 0.8$. A spin polarization mechanism even with a dihedral angle dependence ($a_\alpha{}^H = nB'\rho_S\langle\cos^2\theta\rangle$; $n = 1$ or 2) cannot yield reasonable values of $\langle\cos^2\theta\rangle$.

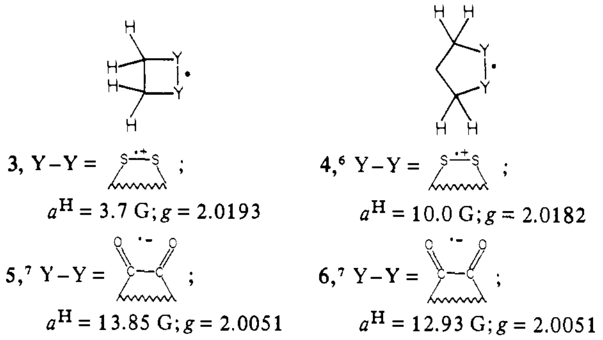


1
$a^H = 5.65\ (6\ H),\ 3.50\ (4\ H)$ G



2
$a^H = 24.2\ (1\ H),\ 8.5\ (4\ H)$ G

Delocalization also explains a puzzling effect of ring size on $a_\alpha{}^H$ for the radical cations **3** and **4** when compared with the semidiones **5** and **6**. In **3** and **4** the unpaired electron is in an antisymmetric MO ($c_{S(i)} = -c_{S(j)}$), whereas the semidiones possess a symmetric SOMO. The value of $a_\alpha{}^H$ will be determined by the hyperconjugative 1,2 interactions and the homohyperconjugative (W plan) 1,3 interactions[8] and will qualitatively be a function of $(c_i\cos\theta_i + \lambda c_j\cos\theta_j)^2$, where i and j are atoms with π-electron spin density α and β to the C–H bond. In the semidiones the symmetric SOMO leads to a reinforcement of the interactions,



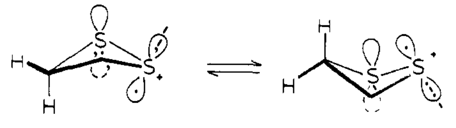
3, Y–Y = ; $a^H = 3.7$ G; $g = 2.0193$

4,[6] Y–Y = ; $a^H = 10.0$ G; $g = 2.0182$

5,[7] Y–Y = ; $a^H = 13.85$ G; $g = 2.0051$

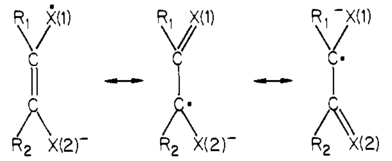
6,[7] Y–Y = ; $a^H = 12.93$ G; $g = 2.0051$

whereas in the 1,2-dithia radical cations the two effects are opposed.[9] Apparently **3** possesses a superior geometric arrangement for the 1,3 interaction in **7** ⇄ **8**.



7 **8**

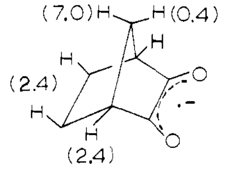
In a related study we have investigated the effect on spin delocalization by replacing semidione oxygen atoms with sulfur atoms (**9** → **10** → **11**). Consistent results were obtained with



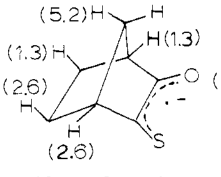
a b c

9, X(1) = X(2) = O
10, X(1) = O; X(2) = S
11, X(1) = X(2) = S

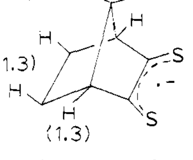
$R_1 = R_2 = CH_3$, $-(CH_2)_4-$, or *cis*-1,3-cyclopentadiyl and $R_1 = C_2H_5$, $R_2 = CH_3$. Replacement of oxygen by sulfur lowers $\rho_{C=X}{}^C$ by approximately 50% as illustrated by the hfs constants for **12**–**14** (a^H in G in Me_2SO). The spin distribution in **11** favors structure **a** over **b** = **c** when X is changed from O to S, presumably because the π-bond energy of C═S is lower than C═O. In **10**, $\rho_{C=S}{}^C > \rho_{C=O}{}^C$ for the same reason, i.e., structure **b** is preferred to **c**.



12,[8] $g = 2.0050$



13, $g = 2.0100$



14, $g = 2.0166$

Radical cations **1**–**4** were observed upon treatment of 2,3-dihydro-5,6-dimethyl-1,4-dithiin (**1**), 2-methyl-4,5-tetramethylene-1,3-dithiole (**2**), 1,2-ethanedithiol or poly(dithio-1,2-ethanediyl) (**3**), and 1,3-propanedithiol or 1,2-dithiolane (**4**) with concentrated H_2SO_4 at 25 °C. The radical cation **3** was initially observed but upon standing the ESR signal was dominated by the $\Delta^{2,2'}$-bi-1,3-dithiolane radical cation.[2,3] Thiosemidiones were formed by the treatment of the 2-mercapto ketones or generated in situ enedithiols with $KOCMe_3$ in Me_2SO at 25 °C.

Registry No. 1, 81195-29-1; **2**, 81195-30-4; **3**, 81195-31-5; **4**, 66609-63-0; **13**, 81195-32-6; **14**, 81195-33-7.

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