Phys. Chem., **23**, 239 (1972).
(26) R. G. Bergman, "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, pp 191-237; M. Schneider and H. Strohäcker, *Tetrahedron*, **32**, 619 (1976).

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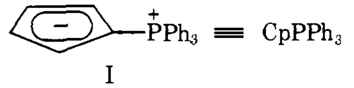
The Synthesis and Structure of Mercuric Halide Complexes of Triphenylphosphonium Cyclopentadienylide. The First X-ray Structure of a Mercury Cyclopentadienyl

Sir:

We wish to report the synthesis and characterization of the initial examples of a new class of metallocenes, the cationic metal halide complexes of triphenylphosphinium cyclopentadienylide, I.



I

Stirring 0.2401 g (0.736 mmol) of $CpPPh_3$ with 0.3360 g (0.738 mmol) of mercuric iodide in 50 ml of dry, deoxygenated (N_2) tetrahydrofuran (THF) at room temperature resulted in the formation of a dark yellow precipitate after a few minutes. Upon filtration 0.3155 g (55%) of the 1:1 adduct, $CpPPh_3HgI_2$, mp 191-192 °C dec, was obtained. More of the product could be precipitated by addition of petroleum ether (60-90 °C), but it was of slightly lesser quality. The complex has been air-stable at room temperature for more than a year. Anal. Calcd for $C_{23}H_{19}HgI_2P$: C, 35.35; H, 2.46; Hg, 25.69; I, 32.51; P, 3.97. Found: C, 35.46; H, 2.61; Hg, 25.38; I, 32.27; P, 2.96. NMR ($CDCl_3$) 6.33-6.72 (m, 4 H, Cp), 7.48-4.98 (bs, 15 H, phenyl); IR (KBr) 1350, 1110, 1080, 1008, 837, 805, 760, 700, 555, 537, 520; λ_{max} (THF) 2400 (17 200), 2500 (19:200), 2640 sh (13 300), 2890 (4000).

By identical procedure the mercury(II) bromide (mp 188-189 °C dec) and chloride (mp 183-184 °C dec) complexes were prepared. Both display long-term stability in the solid form.

The nature of the metal-cyclopentadienyl interaction in complexes of CpHgX (X = Cl, Br, and Cp) has been a subject of debate for nearly 2 decades; both fluxional σ-bonding and π-bonding have been argued.[1] Evidence clearly favors the former view,[2] but the most direct probe, namely, x-ray diffraction, has been frustrated by the inability to grow light-stable single crystals. This has now been accomplished for the mercuric iodide complex of I.

Automated x-ray diffractometer single-crystal measurements were made of 4052 independent reflections of a yellow crystal of $[(C_6H_5)_3PC_5H_4HgI_2]_2$: triclinic, $P\bar{1}$, a = 10.786 (2) Å, b = 11.412 (2) Å, c = 11.016 (2) Å, α = 116.01 (2)°, β = 104.93 (2)°, γ = 92.60 (2)°, Z = 1. Full-matrix least-squares refinement of a model with 154 parameters (Hg, I, P. and C atoms of the cyclopentadiene ring anisotropic) gave R_1 = 0.060, R_2 = 0.052. A drawing of the structure (neglecting the phenyl groups) is shown in Figure 1. The compound exists as a dimer bridged by two iodine atoms, Hg-I (1) distances 2.982 (1) and 2.937 (1) Å, external Hg-I (2) distance 2.681 (1) Å. The phosphorus atom is attached to the cyclopentadiene ring at C(1), (P-C(1), 1.748 (7) Å, C(1) has triangular planar coordination) and the Hg atom is attached at C(3) (Hg-C(3), 2.292 (8) Å, C(3) has tetrahedral coordination). The cyclopentadiene ring distances, C(1)-C(2), 1.375 (10), C(2)-C(3), 1.429 (10), C(3)-C(4), 1.432 (12), C(4)-C(5), 1.367 (11), C(5)-C(1), 1.467 (10) Å, imply double bonds localized at C(1)-C(2) and C(4)-C(5). The bond angles about C(1) (125.2 (6)°, 125.5 (6)°, 109.0 (6)°, sum = 359.7°) are very similar to those found for the triphenylphosphonium cyclopentadienylide ylide.[3] The P-C distance is longer in the mercury substituted ylide (1.748 (7) vs. 1.718 (3)), but the double bond distances in the ring, though nominally shorter (1.375 (10) and 1.367 (11) vs. 1.392 (4) and 1.376 (4) Å for the $CpPPh_3$ ylide), are not significantly different. The coordination about the Hg atom is essentially tetrahedral, with the main distortions being the bridging iodine angles (I(1)-Hg-I(1′), 93.76 (2)°) and angle involving the Cp group (C(3)-Hg-I(2), 131.5 (2)°).

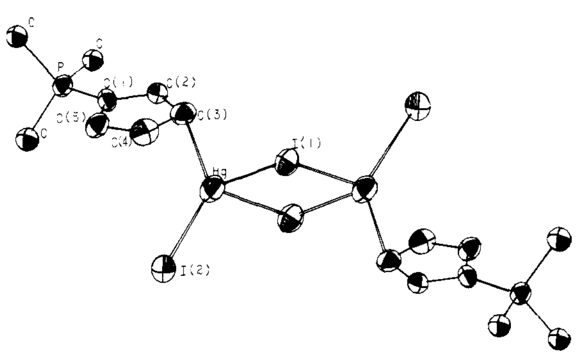


Figure 1. ORTEP of $[(C_6H_5)_3PC_5H_4HgI_2]_2$.

Table I. ^{13}C NMR Chemical Shift Data for Mercury(II)-Ylide Complexes

Compound	Solvent	Cyclopentadienyl chemical shifts (ppm)[a]		
		C(1)	C(2),C(5)	C(3),C(4)
$CpPPh_3$	$CDCl_3$	127	116.9	114.3
$CpPPh_3HgI_2$	$CDCl_3$	—	121.5	111.9
$CpPPh_3HgCl_2$	Me_2SO-d_6	—	123.5	110.8

[a] Center of the ^{31}P-^{13}C splitting pattern (C-H decoupled).

Attachment of the mercury at the 3-position is somewhat of a surprise because C(1) is actually the position of greatest electron density,[4] and C(2) is the position of bonding suggested by superdelocalizabilities (S_E), localization energies (L_r), and the free valences (F_r) of the reaction intermediate in electron transfer theory.[4] In agreement with these reaction indices, electrophiles and even Diels-Alder dienophiles result in substitution at the 2-position. There are no previous examples of reaction at C(3). A possible explanation lies in the steric interaction between the bulky triphenylphosphonium group and the metal halide.[5]

The ^{13}C NMR spectra reveal much about the structure of the mercury complexes in solution (Table I). The mercury is bound to the cyclopentadienyl site and not the phenyls; this is evidenced by the greater chemical shifts (upfield and downfield) of the cyclopentadienyl carbons compared to the phenyl carbons, and the broadening and diminution of the cyclopentadienyl signals. The C(1) absorption of the mercury complexes apparently falls in the phenyl region as all attempts to locate it have been unsuccessful. It is clear that in solution mercury does not remain limited in its attachment to C(3); the fact that both C(2) (and C(5)) and C(3) (and C(4)) are nearly equally broadened and diminished argues for either σ-fluxional or π-bonding. The observation that C(2) and C(3) display chemical shifts in opposite directions argues against π-bound Mulliken-type outer complexes similar to the central-bound (arene)$Cr(CO)_3$.[6] For these reasons, we favor fluxional σ-bonding. Furthermore, the small upfield shift by C(3) would suggest that mercury is bonding somewhat preferentially at this site.

Further indication of fluxional behavior is demonstrated by the ^1H NMR spectra of $CpPPh_3HgX_2$ (X = Cl, Br, I). The cyclopentadienyl hydrogens remain in the δ 6.0–6.6 region and the "aromatic" appearance of the AA′BB′ pattern of the cyclopentadienyl moiety is evident though the resolution on our 60-MHz instrument was inadequate to determine coupling constants. There is a small halogen-dependent chemical shift (downfield) in the order of Cl > Br > I, with the shift of the cyclopentadienyl protons being greater than that of the phenyl protons.

Additional studies have shown that several other metal halides and carbonyl complexes of $CpPPh_3$ and related ylides are readily formed.

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References and Notes

(1) G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, **2,** 32 (1956); T. S. Piper and G. Wilkinson, *ibid.*, **3,** 104 (1956); H. P. Fritz, *Adv. Organomet. Chem.*, **1,** 239 (1964); A. N. Nesmeyanov, G. G. Dvoryantseva, N. S. Kochetkova, R. B. Materikova, and Yu, N. Schienker, *Dokl. Akad. Nauk SSSR*, **159,** 847 (1964); G. G. Dvoryantseva, K. F. Turchin, R. B. Materikova, Yu. N. Schienker, and A. N. Nesmeyanov, *ibid.*, **166,** 808 (1966); A. N. Nesmeyanov, L. A. Fedorov, R. B. Materikova, E. I. Fedin, and N. S. Kochetkova, *Tetrahedron Lett.*, 3755 (1968).

(2) P. West, M. C. Woodville, and M. D. Rausch, *J. Am. Chem. Soc.*, **91,** 5649 (1969); F. A. Cotton and T. J. Marks, *ibid.*, **91,** 7281 (1969); E. Maslowsky, Jr., and K. Nakomoto, *Inorg. Chem.*, **8,** 1108 (1969); W. Kitching and B. F. Hegarty, *J. Organomet Chem.*, **16,** P39 (1969); F. A. Cotton, D. L. Hunter, and J. D. Jamerson, *Inorg. Chim. Acta*, **15,** 245 (1975); A. J. Campbell, C. E. Cottrell, C. A. Fyfe, and K. R. Jeffrey, *Inorg. Chem.*, **15,** 1326 (1976).

(3) H. L. Ammon, G. L. Wheeler, and P. H. Watts, Jr., *J. Am. Chem. Soc.*, **95,** 6198 (1973).

(4) Z. Yoshida, S. Yoneda, and Y. Murata, *J. Org. Chem.*, **38,** 3537 (1973).

(5) Other complexes displaying fluxional behavior are known to be sensitive to steric effects: B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37,** 2084 (1962); J. S. McKekechnie and I. C. Paul, *J. Am. Chem. Soc.*, **88,** 5927 (1966); T. H. Whitesides and R. A. Rudnik, *Inorg. Chem.*, **15,** 874 (1976).

(6) P. A. W. Dean, D. G. Ibbott, and J. B. Stothers, *Can. J. Chem.*, **54,** 166 (1976); G. A. Olah, S. H. Yu, and D. G. Parker, *J. Org. Chem.*, **41,** 1983 (1976).

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Preparation and Properties of Dinitrogen–Molybdenum Complexes. 5.[1] Conversion of the Coordinated Dinitrogen into a Hydrazone Type N_2CRR' Ligand

Sir:

Recent studies on the dinitrogen complexes of molybdenum, tungsten, titanium, and zirconium have disclosed that the coordinated dinitrogen of these complexes reacts with several reagents such as sulfuric acid,[2] hydrogen halides,[3] alkyl halides,[4,5] benzoyl chloride,[6] or tetrahydrofuran.[7] In a previous paper[8] we reported that *trans*-$[Mo(N_2)_2(dpe)_2]$[9] (dpe = $Ph_2PCH_2CH_2PPh_2$) (**1**) reacts with fluoroboric acid to yield a hydrazide (2−) complex *trans*-$[MoF(NNH_2)(dpe)_2]BF_4$ (**2**) in a good yield.

Table I. Infrared Data of $[MoF(N_2CRR')(dpe)_2]BF_4$[a]

R	R′	ν(C=N), cm^{-1}	ν(C=^{15}N), cm^{-1}
CH_3CH_2	H	1565	1550
C_6H_5	H	1525	
CH_3	CH_3	1585	

[a] KBr disks.

$$trans\text{-}[Mo(N_2)_2(dpe)_2] + HBF_4 \rightarrow trans\text{-}[MoF(NNH_2)(dpe)_2]BF_4 \quad (1)$$

We wish here to describe the reaction of **2** with aldehydes and ketones which affords a new potential method of the conversion of the coordinated dinitrogen to a series of hydrazone type ligands

$$trans\text{-}[MoF(NNH_2)(dpe)_2]BF_4 + RR'C{=}O \rightarrow [MoF(N_2CRR')(dpe)_2]BF_4 + H_2O \quad (2)$$

$$(R = CH_3CH_2,\ R' = H;\ R = Ph,\ R' = H;\ R = R' = CH_3)$$

although Chatt and his co-workers recently prepared the analogous complexes $[WBr(N_2CH_2)(dpe)_2]Br$ from **1** and dibromomethane[5] and $[MBr\{NN{=}CH(CH_2)_3OH\}(dpe)_2]Br$ (M = Mo or W) from **1** and tetrahydrofuran in the presence of methyl bromide[7] under irradiation.

When an excess of propionaldehyde (about 8 mol equiv) was reacted with **1** in dichloromethane at ambient temperature for 30 min, the original orange color of the solution turned brownish green and the addition of hexane afforded *trans*-$[MoF(N_2CHCH_2CH_3)(dpe)_2]BF_4$ as brownish green crystals in 82% yield. Anal. Calcd for $C_{55}H_{54}N_2F_5P_4BMo$: C, 61.81; H, 5.10; N, 2.62. Found: C, 61.52; H, 5.07; N, 2.50. Gas chromatographic analysis of the reaction mixture showed the quantitative formation of water according to eq 2. The infrared spectrum of the complex exhibits an intense band at 1565 cm^{-1} assigned to ν(C=N), which shifts to 1550 cm^{-1} upon ^{15}N substitution. The ^1H NMR spectrum shows a triplet band at 5.4 ppm assigned to methine proton, a multiplet band at 1.4 ppm assigned to methylene protons, and a triplet band at 0.6 ppm assigned to methyl protons in a ratio of 1:2:3, indicating that the complex consists of one isomer, although syn and anti isomers about C=N double bond are possible. The ^{19}F NMR spectrum shows a band at 83.0 ppm above benzotrifluoride assigned to fluoroborate anion and a quintet band at 50.3 ppm (J_{F-P} = 30 Hz) in a ratio of about 4:1. This indicates that the $CH_3CH_2CHN_2$ ligand and fluoride anion are trans to each other.

The reaction of benzaldehyde with **1** also gave an analogous green solid $[MoF(N_2CHPh)(dpe)_2]BF_4$ in 25% yield, although a longer reaction time (about 20 h) was required at ambient temperature compared with propionaldehyde. Anal. Calcd for $C_{59}H_{54}N_2F_5P_4BMo$: C, 63.45; H, 4.88; N, 2.51; F, 8.51; P, 11.09. Found: C, 63.29; H, 4.87; N, 2.56; F, 8.46; P, 11.13. In this case were given red crystals as by-product, which did not contain nitrogen.

In addition to aldehydes, **1** reacted with acetone at a refluxing temperature for 27 h to yield $[MoF(N_2C(CH_3)_2)(dpe)_2]BF_4 \cdot CH_3COCH_3$ as greenish brown crystals in 38% yield. Anal. Calcd for $C_{58}H_{60}N_2OF_5P_4BMo$: C, 61.82; H, 5.38; N, 2.49. Found: C, 62.29; H, 5.42; N, 2.34. Solvating acetone was easily lost on recrystallization from dichloromethane–hexane. This reaction was remarkably accelerated in the presence of an acid, as is usually found in the condensation reaction of aldehydes with hydrazines and amines. Thus, only 1 h of stirring of a mixture of **1** and acetone was enough