Anhydrous aluminum iodide was prepared by standard methods and dissolved in anhydrous ammonia which was also prepared and handled by standard techniques. The Al(III) concentration was *ca.* 1.35 *M*. In other experiments it had been found that addition of $Cu(NH_3)_4(NO_3)_2$ to the extent of *ca.* 0.2 *M* broadened the solvent ammonia line beyond detection (the bound ammonia line and solvent line occur at essentially the same frequency) and that Cu(II) and I^- were stable in ammonia. Addition of the Cu(II) nitrate salt caused precipitation of some Al(III) the amount of which was determined, and an appropriate correction was made. The ^{14}N nmr absorption line for the bound ammonia (and references) was measured at *ca.* 9300 gauss using equipment previously described.[6] The areas under the curves were measured in various ways and compared with areas obtained for standard aqueous $NaNO_2$, $Co(NH_3)_6^{3+}$ in ammonia, $Co(NH_3)_5 \cdot H_2O$ in water, and others. The known solutions gave internally consistent results and were chosen to give line widths and intensities comparable to that found for the Al(III) species. This was done so that all the nmr measurements could be made under essentially identical conditions of radiofrequency level, modulation amplitude, etc. The full width at half-maximum absorption for the bound ammonia line was 1.35 ± 0.14 gauss at 27°. The coordination number of Al(III) was found to be 6.03 ± 0.45 (as an average of four signals).

We were unable to shift the solvent line sufficiently to be useful using either Cu(II) (which produces relatively small shifts) or Co(II) without causing excessively large amounts of broadening. Dysprosium nitrate was found to be too insoluble in ammonia to be useful for shifting the solvent line.

The results imply a relatively long lifetime for the $Al(NH_3)_6^{3+}$ species in ammonia consistent with the results of Sutter and Hunt[7] using ^{15}N tracer techniques. A coordination number of six was also found for the hydrated species.[3] The precision of the measurements was limited because of the broad, weak signals involved. Attempts to measure solvation number for Be(II) and Ga(III) have failed so far because of solubility problems. The use of ^{15}N and improved nmr equipment may make it possible to study other species in the future.

(6) H. H. Glaeser, G. A. Lo, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **4**, 206 (1965).

(7) J. R. Sutter and J. P. Hunt, *J. Am. Chem. Soc.*, **82**, 6420 (1960).

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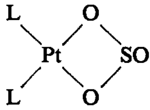
Oxidation of Coordinated Ligands. Sulfato and Nitrato Complexes of Platinum

Sir:

During the recent upsurge in interest in the behavior of d^{10} and d^8 complexes, a variety of working models have been suggested in an attempt to rationalize and predict the chemistry of these species.[1,2] Recently we have inclined strongly to the view that the behavior in solution of the zerovalent complexes $M(PPh_3)_4$ (M = Ni, Pd, Pt) is essentially that of solvated metal atoms. The characteristics[1] of the oxygen and ethylene complexes, $(PPh_3)_2PtO_2$ and $(PPh_3)_2Pt(C_2H_4)$, helped to reinforce this concept and prompted an investigation under homogeneous conditions[3] of those reactions in which platinum has traditionally served as a heterogeneous catalyst; *e.g.*, the contact process.

Passage of SO_2 into a solution of $(PPh_3)_2PtO_2$ at room temperature results in the rapid formation of an air-stable complex which we believe to be the sulfato complex I. *Anal.* Calcd for $C_{36}H_{30}O_4P_2SPt$: C, 53.00; H, 3.68; mol wt, 815. Found: C, 52.92; H, 3.66; mol wt, 795.



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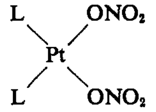

II

L = PPh_3

The infrared spectrum (Nujol) shows four strong band with some splitting at 1279, 1165 and 1150, 880 and 871, and 650 cm^{-1}, which is in accord with the symmetry of the SO_4 group acting as a bidentate ligand (C_{2v}) and is in reasonable agreement with the spectrum reported by Barraclough and Tobe[4] for the complex $[Co(en)_2SO_4]Br$, one of the few monomeric complexes known to contain bidentate sulfate. The possibility of a sulfur-bonded sulfito complex[5] cannot be ruled out in terms of the number of bands observed, but is, we feel, unlikely in view of the high frequency of the band which we assign to the asymmetric S–O stretch (1279 cm^{-1}). Reaction between SO_2 and a solution of the ethylene adduct, $(PPh_3)_2Pt(C_2H_4)$, results in displacement of ethylene and formation of a brown crystalline complex[6] which loses SO_2 readily on warming (50°) to yield the air-stable, green complex $(PPh_3)_2Pt(SO_2)$. *Anal.* Calcd for $C_{36}H_{30}O_2P_2SPt$: C, 55.17; H, 3.83; S, 4.09. Found: C, 54.92; H, 3.94; S, 4.68. Two strong infrared bands (Nujol) are found at 1182 and 1149 and 1035 cm^{-1}, resulting from asymmetric and symmetric S–O stretching vibrations. The spectrum is strongly indicative of a sulfur-bonded SO_2 adduct, and the complex is presumably of a similar type to $(SO_2)IrCl(CO)(PPh_3)_2$ recently reported by Vaska.[7] Passage of oxygen through a solution of the green SO_2 adduct, or heating the complex in air (110°), results in the formation of the sulfato complex already described.

Similar results are obtained when the oxygen adduct is treated with NO_2, the dinitrato complex (II) being obtained pure and in high yield. *Anal.* Calcd for $C_{36}H_{30}N_2O_6P_2Pt$: C, 51.25; H, 3.56; N, 3.32. Found: C, 51.43; H, 3.65; N, 3.16. The complex

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(1) C. D. Cook and G. S. Jauhal, *Inorg. Nucl. Chem. Letters*, **3**, 31 (1967).

(2) J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **88**, 3459 (1966).

(3) It has recently been shown by G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem. Intern. Ed. Engl.*, **6**, 92 (1967), that a solution of complex $(PPh_3)_2NiO_2$ functions as a catalyst for the oxidation of triphenylphosphine.

(4) C. G. Barraclough and M. L. Tobe, *J. Chem. Soc.*, 1993 (1961).

(5) G. Newman and D. B. Powell, *Spectrochim. Acta*, **19**, 213 (1963).

(6) We have learned of closely related experiments by J. J. Levison and S. D. Robinson, *Chem. Commun.*, 198 (1967), following submission of this paper. They report the preparation of the brown, apparently four-coordinated adduct, $(PPh_3)_3PtSO_2$, and its ready oxidation to the sulfato complex, $(PPh_3)_2PtSO_4$, described herein.

(7) L. Vaska and S. S. Bath, *J. Am. Chem. Soc.*, **88**, 1333 (1966).

absorbs strongly at 1502 and 1491, 1272 and 1263, 974, and 787 cm^{-1} in the infrared (Nujol) and is evidently comparable to a series of four-coordinate dinitrato complexes reported by Bannister and Cotton.[8]

The dinitrato complex is decomposed rapidly by boiling water with the liberation of nitrate ion; the sulfato complex is considerably more resistant to hydrolysis, but reaction with cyanide ion results in displacement of the coordinated sulfate group and formation of a cyano complex of Pt(II) (infrared band at 2132 cm^{-1}).

The mechanistic aspects of some of these reactions are currently receiving attention.

Acknowledgment. We thank the National Research Council of Canada and Engelhard Industries (Canada) Ltd. for their support.

(8) E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 2276 (1960).

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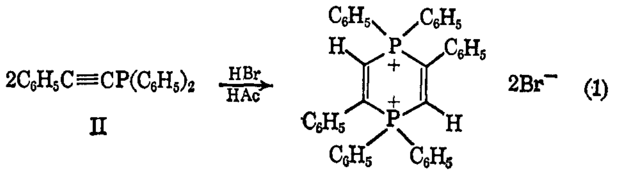
Delocalization of the π-Electron System in 1,4-Dihydrophospha(V)pyrazines

Sir:

The nature of π-electron delocalization in the phosphonitrilic system has been the subject of some controversy.[1,2] The few cyclic phosphorus–carbon six-π-electron systems capable of 3d–2p π delocalization thus far synthesized have been rather unstable.[3,4]

We wish to report the synthesis of a stable 1,4-dihydrophospha(V)pyrazine in which there appears to be delocalization of the four π electrons over the phosphorus atoms.

We have isolated 1,1,2,4,4,5-hexaphenyl-1,4-diphosphoniacyclohexadiene-2,5 dibromide (Ia) in over 60% yield from the 100-hr reaction of phenylethynyldiphenylphosphine[5] (II) with hydrogen bromide in glacial acetic acid at room temperature (eq 1). The orange solid



(1)

Ia

Ia melted at 286–290° (from ethyl acetate–methanol). *Anal.* Calcd for $C_{40}H_{32}P_2Br_2 \cdot H_2O$: C, 63.83; H, 4.52; P, 8.24; Br, 21.28. Found: C, 63.85; H, 4.49; P, 8.30; Br, 21.05.

The water solubility, the infrared spectrum, and the fact that it gives an immediate yellow precipitate (Ib) when treated with aqueous sodium picrate show that Ia is a phosphonium salt.

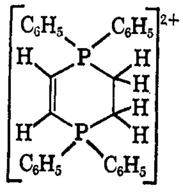
Elemental analysis establishes Ia as a 1:1 adduct of II and HBr, *i.e.*, $[(C_6H_5)_2PC{\equiv}CC_6H_5 \cdot HBr]_n$, while the lack of covalently bound bromine in the adduct is deduced from the analysis of the picrate Ib, mp 245–248° (from acetonitrile). *Anal.* Calcd for $C_{52}H_{36}N_6O_{14}P_2$: C, 60.58; H, 3.50; N, 8.16; Br, 0.00. Found: C, 60.50; H, 3.37; N, 8.14; Br, 0.00.

Table I[a]

Compd	Protons	Multiplicity	J_{P-H}, cps	τ, ppm	Area ratio
Ia	Vinyl	1 Broad complex 1		0.60 1.04 1.5	1
	Phenyl-P	Complex		2.0	10
	Phenyl-C	1		2.38	5
IIIa	CH	Complex		~4.6	1
	Phenyl	Complex		~2.2	15
	CH_2	Complex		~5.6	2
IV	Vinyl	1 Broad complex 1		1.00 1.42 1.84	1
	Phenyl-P	Complex		2.15	10
	CH_2	2 (broad)	8.0	6.11	2

[a] Proton nmr at 60 Mc/sec employing tetramethylsilane as an internal standard and trifluoroacetic acid as solvent.

The proton nmr spectrum of a trifluoroacetic acid solution of Ia at 60 Mc (Table I) shows two sharp peaks at τ 0.6 and 1.5 with a shallow broad complex centered between them. This is similar to the proton nmr spectrum of 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexene-2 dibromide (IV)[6] (Table I). These data fit a polymeric vinylenebis(diphenylphosphonium) bromide.



IV

$$-\!\!\!\!\left[P(C_6H_5)_2CH{=}C(C_6H_5)\right]\!\!\!\!-_n{}^{n+} \quad nBr^-$$

Furthermore, the melting point and complete absence of covalently bound bromine strongly suggest a cyclic structure in which n is not very large.

Osmotic pressure depression of methanol solutions of Ia over a range of concentrations (Table II) showed that association occurs at higher concentrations and that the effective molecular weight, obtained by extrapolation, approaches the value of 245 (where n = 2).

Table II. Molecular Weight Determination of Ia in Methanol Solution by Osmometric Method

Concentration		
mg/ml	M	Mol wt
9.470	0.0320	296
5.995	0.0212	283
3.280	0.0123	267

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(1) D. P. Craig and N. L. Paddock, *Nature*, **181**, 1052 (1958); *J. Chem. Soc.*, 4118 (1962).

(2) M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *ibid.*, 2423 (1960).

(3) G. Markl, *Angew. Chem.*, **75**, 168 (1963); **75**, 669 (1963); *Z. Naturforsch.*, **18b**, 1136 (1963).

(4) E. A. Cookson and P. C. Crofts, *J. Chem. Soc., Sect. C*, 2003 (1966).

(5) W. Chodkiewicz, P. Cadiot, and A. Willemant, *Compt. Rend.*, **250**, 866 (1960); K. Issleib and G. Harzfeld, *Chem. Ber.*, **95**, 268 (1962).

(6) A. M. Aguiar and H. J. Aguiar, *J. Am. Chem. Soc.*, **88**, 4090 (1966).