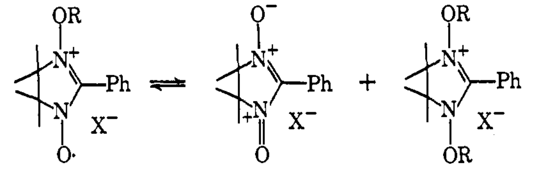
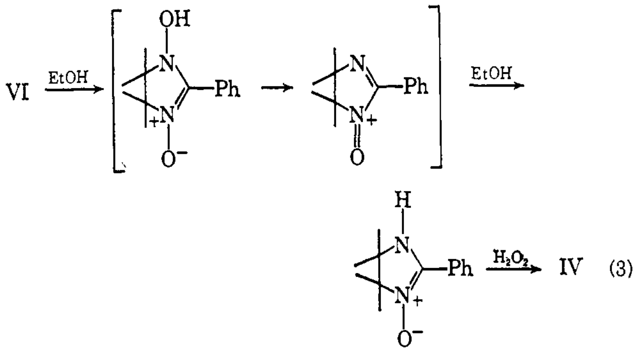
only a reduced-intensity esr signal identical with that of an aqueous solution of the starting radical IV rather than the protonated species V (R = H). Since neutralization of these solutions in each case quantitatively regenerated radical IV, these observations suggest a disproportionation process such as (2) (R = H or $COCF_3$) which is favored with trifluoroacetic anhydride or aqueous acid but not with nonaqueous acid.



(2)

V VI VII

Further evidence for the disproportionation reaction was found by comparison of the properties of acidic solutions of IV with those of the reaction product of IV with chlorine. Thus, solutions of IV in carbon tetrachloride after treatment with chlorine gas and evaporation of the solvent yielded an orange solid, VI (X = Cl) [τ 2.34 (5-ArH) and 8.17 (singlet, 4-CH_3) (SO_2Cl_2); ν^{KBr} 1600 (w), 1580 (w), and 1140 cm^{-1}]. Both this compound and strongly acidic solutions of IV were exceptionally powerful oxidants. They not only readily oxidized aqueous iodide or bromide with liberation of the free halogens but also attacked many organic compounds and most solvents. Indeed, VI was even reduced slowly by water, and it was also found to oxidize aqueous alkali to hydrogen peroxide, although acidic solutions of IV failed to do this, apparently because of the rapid reversal of the disproportionation process (2) on neutralization. Parallel reactions of VI in neutral ethanol and of the radical IV in 1 *N* ethanolic hydrochloric acid were also observed. Both solutions became colorless on boiling for a few minutes, and good yields (60–80%) of a new product, VIII, were obtained. Structure VIII is supported by its spectral data which suggest the existence of intermolecular association even in dilute solutions [ν^{CHCl_3} 3380, 3130, 2500, 2350, 1600 (w), 1572 (w), and 1150 cm^{-1}; τ 1.72 (2 *o*-ArH), 2.2 (3 ArH), 6.08 (1 NH, broad), 8.67 (2-CH_3), and 8.72 (2-CH_3) (EtOH); $\lambda_{\max}^{\text{EtOH}}$ 238 mμ (ϵ ~15,000) and 325 (~5000) (concentration dependent)] and by its oxidation by hydrogen peroxide and phosphotungstic acid back to the radical IV.



(3)

VIII

Condensation of the bishydroxylamine I has also been found to proceed with other aromatic aldehydes as, for example, *p*-hydroxy- and *p*-nitrobenzaldehydes. The corresponding nitronyl nitroxide radicals had esr spectra in benzene that were very similar to that of IV (a_N = 7.5 gauss, g = 2.00660 and 2.00645 ± 0.00003, respectively) and their mass spectra likewise showed intense molecular ion peaks. Aliphatic derivatives of IV are also readily prepared, and future communications will deal with the chemistry of these and related radicals.

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Lewis Acid Adducts of Planar Four-Coordinated d^8 Complexes. BF_3-$[IrClCO(P(C_6H_5)_3)_2]$ and Related Systems

Sir:

Although the basicity of certain metal complexes toward molecular Lewis acids is now recognized,[1,2] unequivocal examples are lacking for adducts of four-coordinated planar d^8 complexes with σ Lewis acids like BF_3.[3] Schrauzer published the first attempt to bring about donor–acceptor interaction between BF_3 and a planar d^8 complex.[4] This work with a Ni(II) complex and other studies with Ni(II) and Pd(II) complexes led to no observable metal basicity.[5]

Rapid tensimetric titration of the planar d^8 complex $[IrClCO(P(C_6H_5)_3)_2]$[6] (**1**), in benzene solution at 5.5°, led to a break in the pressure–composition curve at $2BF_3{:}1Ir$ complex. Also, a slow secondary reaction was observed which resulted in uptake beyond the 2:1 stoichiometry. Cryoscopic molecular weight determinations for *ca.* 5 m*M* solutions of the 2:1 complex in benzene gave an average molecular weight of 1150 as compared with the formula weight of 916 (the experimental value is thought to be slightly high because of traces of precipitate which formed even at these low concentrations). The solid 2:1 adduct has a single CO stretching frequency at 2063 cm^{-1} which is 107 cm^{-1} higher than ν_{CO} of the parent complex; it also contains BF stretching bands characteristic of tetrahedrally coordinated boron (1138, 931, and 960 cm^{-1}) but none in the region expected for three-coordinated boron (1200–1450 cm^{-1}). The BF_3 stretches are quite different from those of $(C_6H_5)_3PBF_3$ (1150–1000, 915, 888 cm^{-1}). The Ir–Cl stretching frequency is 325 cm^{-1}, a value which is very slightly higher than in the parent complex (321 cm^{-1}).

Attempts to isolate a solid 1:1 complex by mixing stoichiometric quantities of BF_3 and **1**, followed by removal of the benzene solvent, always resulted in a product displaying sharp absorptions of nearly equal intensities at 1956 and 2063 cm^{-1}, attributable to

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[1] M. P. Johnson and D. F. Shriver, *J. Am. Chem. Soc.*, **88**, 301 (1966), and references therein.

[2] L. Vaska and D. L. Catone, *ibid.*, **88**, 5324 (1966).

[3] A possible exception is the report that BCl_3 and BBr_3 adducts of a Rh(I) complex may be prepared: P. Powell and H. Nöth, *Chem. Commun.*, 637 (1966).

[4] G. N. Schrauzer, *Ber.*, **95**, 1438 (1962).

[5] D. F. Shriver, *J. Am. Chem. Soc.*, **84**, 4610 (1962); **85**, 1405 (1963); D. F. Shriver, A. Luntz, and J. J. Rupp, Proceedings of the 8th International Conference on Coordination Chemistry, Vienna, Sept 1964.

[6] L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961).

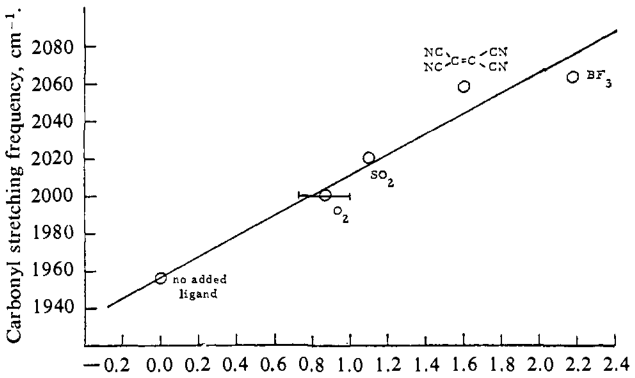

Figure 1. Carbonyl stretching frequencies of $[IrCOCl(PPh_3)_2]$ and its adducts *vs.* electron affinity of added ligand. Except for the BF_3 adduct all infrared data are taken from the literature.[10,12] The molecular electron affinities for O_2, SO_2, and BF_3 are those reported by V. I. Vedeneyev, *et al.*, "Bond Energies, Ionization Potentials and Electron Affinities," Arnold, London, 1966. For TCNE the value is from G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

$[IrClCO(P(C_6H_5)_3)_2]$ and its bis(boron trifluoride) adduct.[7] However, formation of the 1:1 complex in solution is clearly indicated by titrations in which composition of the benzene solution is monitored by infrared or near-ultraviolet spectroscopy. At a composition of $1.2BF_3$:1Ir complex the 1968-cm⁻¹ band of the parent complex has disappeared and a single new CO stretching frequency has taken its place at 2067 cm⁻¹. When the reaction is followed under experimentally more favorable conditions (dilute solution at 387 mμ), the mole ratio at the end point is much closer to 1:1 ($1BF_3$ per 1.021). The molecular weight of the 1:1 adduct, as indicated by cryoscopy in benzene solution, is 900 *vs.* the formula weight of 848. Thus, although a 1:1 complex is formed in solution, it appears to disproportionate upon removal of solvent.

In view of the molecular weight and CO stretching frequency, the two most likely modes of attachment of BF_3 to the Ir complex for 1:1 adduct are (1) simple Ir–B donor–acceptor interaction or (2) oxidative insertion of the Ir atom into a B–F bond.[8]

The former possibility is favored because (1) there is evidence against oxidative insertion in the case of the 2:1 adducts (*i.e.*, no trigonally bonded boron is present), (2) the parent complex, **1**, can be regenerated by treating the adduct with mild bases such as acetone or amines, and (3) $B(C_6F_5)_3$, which is similar in acidity to BF_3[9] but for which insertion is unlikely, forms a weak adduct with $[IrClCO(P(C_6H_5)_3)_2]$. This adduct displays a CO stretching frequency similar to that of the BF_3 adduct. (Furthermore, the more stable $[IrClCO(P(C_2H_5)_2C_6H_5)_2]\cdot B(C_6F_5)_3$ yields a ^{19}F nmr spectrum which is characteristic of a simple $B(C_6F_5)_3$ adduct and not an insertion product.) Since the CO stretching frequencies are nearly identical for the 1:1 and 2:1 adducts, it is probable that the second molecule of BF_3 is not attached directly to Ir, but the true nature of the 2:1 adduct is not clear.

In Figure 1 the carbonyl stretching frequencies of several molecular adducts and the uncoordinated iridium(I) complex are plotted as a function of the electron affinity of the added molecule.[10] There is a roughly linear dependence of the stretching frequency upon the electron affinity indicating that the electron density around the iridium atom decreases in a smooth continuous fashion rather than in discrete discontinuous jumps between the formal oxidation states I, II, and III.

It has been pointed out[11–13] that O_2, $C_2(CN)_4$, and SO_2 can form bonds to iridium in which two types of interactions can occur. These are weak donation from filled π orbitals in O_2 and $C_2(CN)_4$ or the nonbonding electron pair on the sulfur atom in SO_2, and moderately strong acceptance of electron density from the metal by a π-bonding interaction of filled metal d orbitals and antibonding orbitals on the ligand molecules. In the case of the boron trifluoride adduct, the only possible interaction is σ donation from iridium to boron. The correlation of the carbonyl stretching frequencies with molecular electron affinities for the added molecules, including BF_3, suggests that all of the molecular adducts considered here may be viewed as Lewis salts in which the metal primarily serves as a donor. Accordingly, much of the chemistry of the Ir(I) adducts can be described in terms of the strongest electron acceptor (Lewis acid) forming the most stable complex. Thus, the uptake of O_2 and of SO_2 by $[IrClCO(P(C_6H_5)_3)_2]$ is reversible, while BF_3 uptake is not. Similarly, C_2F_4 is more strongly[14] held than C_2H_4. However, some caution is necessary in the inference of Lewis acid strengths from known or estimated electron affinities, or even from acidity toward radically different reference bases. For one thing the three-center bonds formed between the oxygen-like acids and the metal are different in detail from the two-center boron–metal bond. Also differences may occur in the geometry of the first coordination sphere and in the degree of reorganization of the acid. Therefore, comparisons of stabilities with electron affinities or of frequencies with electron affinities are only potentially meaningful for large differences.[15]

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(7) Solvent removal was performed on the vacuum line which allowed a check of all volatiles removed from the reaction mixture. This experiment demonstrated that no BF_3 was evolved from the 1:1 mixture.

(8) G. Schmid, W. Arloth, and H. Nöth, *Angew. Chem. Intern. Ed. Engl.*, **6**, 696 (1967).

(9) A. G. Massey and A. G. Park, *J. Organometal. Chem.* (Amsterdam), **5**, 218 (1966).

(10) It is to be emphasized that upon interaction with the iridium complex, cleavage of the added molecule does not occur for any of the cases cited in Figure 1.

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

(12) J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *Science*, **155**, 709 (1967).

(13) W. H. Baddley, *J. Am. Chem. Soc.*, **88**, 4545 (1966).

(14) R. Cramer and G. W. Parshall, *ibid.*, **87**, 1392 (1965).

(15) Supported by the National Science Foundation through Grant GP-6676.

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Trimethylsilyldiazomethane and Trimethylsilylcarbene

Sir:

A recent report on "trimethylstannyldiazomethane"[1] mentioned in passing that trimethylsilyldiazomethane