parently adds to alkynes with the same Markovnikov-type orientational preference exhibited by alkanesulfenic acids.[2]

Pyrolysis of neat **2** at 96° for 7 hr gave isobutylene in 45% isolated yield,[9] water, di-*tert*-butyl polysulfides (disulfide, trisulfide, and tetrasulfide, in molar ratios of *ca.* 1:6:6, representing 44 mol % of isolated products; characterized through comparison with authentic materials), and a colorless, waxy solid identified as t-BuSO$_2$SSBu-t (**6**; 7 mol % of isolated products).[10] Decomposition of dilute (10^{-2} *M*) solutions of **2** in heptane at 75° and 96° gave good unimolecular kinetics for the disappearance of **2**.

The pyrolysis of di-*tert*-butyl sulfoxide is reported to give *tert*-butanesulfenic acid, *t*-BuSOH, and this latter compound is said to dehydrate to thiolsulfinate **2** (eq 3 and 4).[11] Our results indicate that **2** on pyrolysis may also undergo elimination of isobutylene giving a compound which, on the basis of trapping studies (the results of which closely parallel analogous studies with alkanesulfenic acids[2])[11] and by analogy to the elimination reaction of eq 3, may be formulated as *tert*-butanethiosulfoxylic acid, *t*-BuSSOH (**1**; eq 5). The isolation of water from the pyrolysis of **2** suggests that *t*-BuSSOH may also undergo an intermolecular dehydration (eq 6) analogous to *t*-BuSOH (eq 4) affording sulfinyl compound **7**, which may be a precursor to the observed pyrolysis products of **2**.[12,13]

$$t\text{-BuS(O)Bu-}t \xrightarrow{\Delta} t\text{-BuSOH} + (CH_3)_2C{=}CH_2 \qquad (3)$$

$$2t\text{-BuSOH} \longrightarrow \underset{\mathbf{2}}{t\text{-BuS(O)SBu-}t} + H_2O \qquad (4)$$

$$\underset{\mathbf{2}}{t\text{-BuS(O)SBu-}t} \xrightarrow{\Delta} \underset{\mathbf{1}}{t\text{-BuSSOH}} + (CH_3)_2C{=}CH_2 \qquad (5)$$

$$\underset{\mathbf{1}}{2t\text{-BuSSOH}} \longrightarrow \underset{\mathbf{7}}{t\text{-BuSS(O)SSBu-}t} + H_2O \qquad (6)$$

Finally, our results in this and the preceding paper may offer an explanation for the particularly effective inhibitory action of **2** and other dialkyl thiolsulfinates on the reaction of squalene with oxygen and on certain autoxidation processes.[14] From the data of Barnard,[14] it appears that the inhibitory action of **2** at 75° directly parallels the thermal formation of thiosulfoxylic acid **1** from thiolsulfinate **2** (eq 5); a similar parallel would appear to exist between the inhibitory action of alkyl thiolsulfinates possessing α-sulfenyl protons and the production of alkanesulfenic acids according to eq 1. We suggest that sulfenic and thiosulfoxylic acids, thermally produced from alkyl thiolsulfinates according to eq 1 and 2, are the active antioxidants, rather than the thiolsulfinates themselves.[15,16]

Acknowledgment. We thank Mr. Daniel Kleypas for technical assistance and gratefully acknowledge support from the donors of the Petroleum Research Fund administered by the American Chemical Society (Grants 1153-G and 4109-B), the Air Pollution Control Office, Environmental Protection Agency (AP-1496-01), and the University of Missouri, St. Louis.

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had ions at *m/e* 222 ($C_8H_{14}S_2O_3$, parent), 166 (P − C_4H_8), 134 (P − C_4H_8S), 89, 57 (base), and 41. Compound **5** had uv λ_{max} (ethanol) at 261 nm (ε 2960). *Anal.* Calcd for **3**, $C_{12}H_{16}S_2O$: C, 59.96; H, 6.71; S, 26.68. Found: C, 59.39; H, 6.66; S, 26.90. Calcd for **4**, $C_8H_{14}S_2O_3$: C, 43.22; H, 6.35; S, 28.84. Found: C, 43.99; H, 6.46; S, 29.04. Calcd for **5**, $C_{11}H_{22}S_2O$: C, 56.36; H, 9.46. Found: C, 56.82; H, 9.84.

(8) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959.

(9) Constituted 49 mol % of isolated products; gas-phase ir spectrum superimposable on that of authentic isobutylene.

(10) Compound **6** had mp 56–60° after recrystallization from pentane; nmr (CCl$_4$) had singlets of equal integrated areas at δ 1.42 and 1.47, precluding a symmetrical (RS)$_2$SO$_2$ structure; ir spectral bands at 7.64 and 9.00 μ (sulfonyl group). Parent ion in mass spectrum at *m/e* 242. *Anal.* Calcd for $C_8H_{18}S_3O_2$: C, 39.63; H, 7.48. Found: C, 39.78; H, 7.55.

(11) J. R. Shelton and K. E. Davis, *J. Amer. Chem. Soc.*, **89**, 718 (1967).

(12) Various cross dehydration products involving *tert*-butanesulfenic acid and *tert*-butanethiosulfoxylic acid (**1**) may also be formed during the pyrolysis of di-*tert*-butyl sulfoxide.

(13) See J. L. Kice, *Accounts Chem. Res.*, **1**, 58 (1968), for a discussion of electrophile–nucleophile catalyzed reactions of thiolsulfinates and related sulfinyl compounds leading to products at the disulfide and thiolsulfonate oxidation states. Also see ref 1b.

(14) D. Barnard, L. Bateman, and J. I. Cunneen, "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, Chapter 21; D. Barnard, L. Bateman, M. E. Cain, T. Colclough, and J. I. Cunneen, *J. Chem. Soc.*, 5339 (1961); L. Bateman, M. Gain, T. Colclough, and J. I. Cunneen, *ibid.*, 3570 (1962).

(15) It is possible that a fraction of the antioxidant activity of alkyl thiolsulfinates may reflect direct interaction of the thiolsulfinate with peroxy radical or hydroperoxides, as suggested by Barnard.[14] In the case of *t*-BuS(O)SBu-*t*, however, direct interaction is unfavorable on steric grounds.

(16) A similar suggestion has recently been advanced to explain the antioxidant activity of di-*tert*-butyl sulfoxide and sulfinyldipropionate esters: G. Scott, *Mech. React. Sulfur Compounds*, **4**, 99 (1969); C. Armstrong and G. Scott, *J. Chem. Soc. B*, 1747 (1971).

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Synthesis and Structure of Some Novel Transition Metal Arylazo Complexes Involving Metal–σ-Carbon Bonds

Sir:

Despite the formal analogy between the electronic structures of the nitrosonium (N≡O$^+$) and aryldiazonium (ArN≡N)$^+$ ions, the reactions of the latter with transition metal complexes are providing an increasing assortment of novel products,[1-3] several of which are of current interest in connection with the use of the aryldiazonium function as a model for complexed dinitrogen in the nitrogen fixation process. We have already commented[3] on the synthesis of an iridium–tetrazene complex from one such reaction, and now wish to report the structure of a further novel product obtained from the same reaction.

Deeming and Shaw[4] showed that [IrCl(CO)(PPhMe$_2$)$_2$] would oxidatively add $C_6H_5N_2{}^+BF_4{}^-$ in the presence of LiCl to give [IrCl$_2$($C_6H_5N_2$)(CO)(PPhMe$_2$)$_2$]. However, the reaction of [IrCl(CO)(PPh$_3$)$_2$] with (p-X-$C_6H_4N_2$)$^+BF_4{}^-$ (X = F, Br) in benzene–ethanol, in the absence of LiCl does not result in the salt [IrCl(p-X-$C_6H_4N_2$)CO(PPh$_3$)$_2$]$^+BF_4{}^-$ (**1**) even though the corresponding nitrosyl complex is easily obtained when NO$^+BF_4{}^-$ is employed. Instead, red crystals of the iridium–tetrazene complex crystallize from the deep red solution.[3] We repeated the reaction, this time removing solvent by freeze drying before crystallization

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(1) G. W. Parshall, *J. Amer. Chem. Soc.*, **89**, 1822 (1967).

(2) L. Toniolo and R. Eisenberg, *Chem. Commun.*, 455 (1971).

(3) F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner-Canham, and D. Sutton, *J. Amer. Chem. Soc.*, **93**, 1826 (1971).

(4) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1128 (1969).

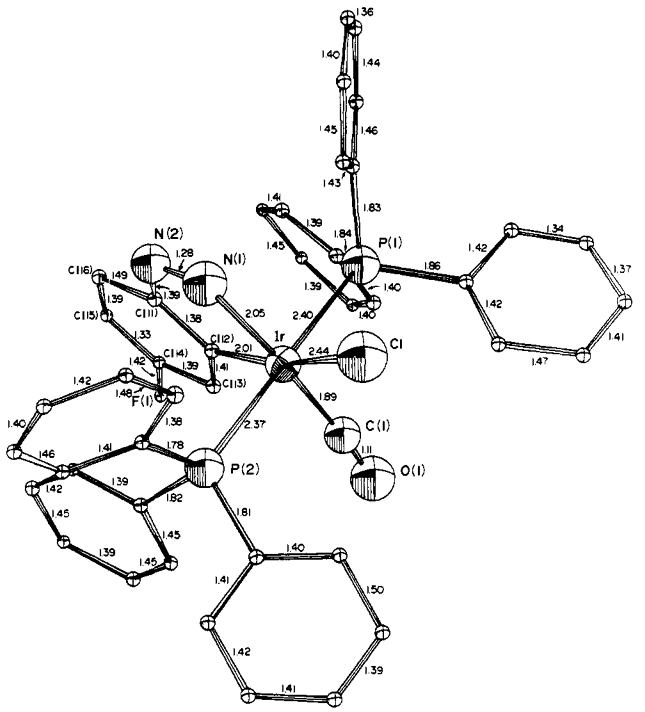
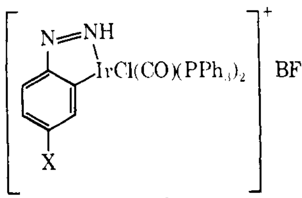


Figure 1. Molecular configuration of the cation $[Ir(FC_6H_3NNH)Cl(CO)(PPh_3)_2]^+$. Estimated standard deviations in bond lengths are: Ir–P(Cl), 0.01 Å; Ir–C (or N), 0.03 Å; C(or N)–N, 0.04 Å, C–C, 0.05 Å. Selected bond angles are (a) around Ir: P-1–P-2 179; P-1–Cl, 89; P-1–N-1, 91; P-1–C-1, 89; P-1–C-12, 89; P-2–Cl, 90; P-2–N-1, 89; P-2–C-1, 91; P-2–C-12, 92; Cl–N-1, 91; Cl–C-1, 98; Cl–C-12, 168; N-1–C-1, 171; N-1–C-12, 78. (b) others: Ir–C-1–O-1, 175; Ir–N-1–N-2, 121; N-1–N-2–C-11, 112°.

occurred, leaving a dark residue. This was stirred with benzene, and the insoluble portion then recrystallized at room temperature from acetone–ether to yield pure yellow crystals of an air-stable, diamagnetic compound **2**. Addition of further ether to the filtrate after removal of **2** gave a mixture of **2** and the tetrazene complex.

Analytically, the product **2** was indistinguishable from the anticipated product **1** or its acetone solvate.



2, X = F, Br

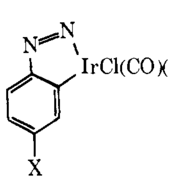
Anal. Calcd for $C_{43}H_{34}N_2OBClF_5P_2Ir \cdot (CH_3)_2CO$: C, 52.70; H, 3.82; N, 2.68. Found (para fluoro complex–acetone): C, 52.65; H, 3.88; N, 2.85. Calcd for $C_{43}H_{34}N_2OBBrClF_4P_2Ir$: C, 49.00; H, 3.23; N, 2.66; Cl, 3.36; Br, 7.58. Found (para bromo complex): C, 48.98; H, 3.25; N, 2.76; Cl, 3.23; Br, 7.56. However, chemical and crystallographic studies have revealed that **2** is an isomer of **1** consisting of the cation illustrated in Figure 1. This cation is structurally derived from the cation of **1** by the apparent migration of H-1 from the ortho position C-12 to N-1 of the arylazo function, thus permitting C-12 to coordinate to the iridium atom and thereby achieve a coordination environment of six about Ir(III).

The ir spectrum of **2** exhibited ν(N–H) at 3150, ν(N═N) at 1415 (*p*-F) and 1407 (*p*-Br), ν(CO) at 2050 (F) and 2054 (Br), and bands at 710, 820, and 865 cm^{-1} which may be due to the 1,2,4-trisubstituted aromatic ring. The assignment of ν(N═N) was confirmed by ^{15}N substitution at N-1 in the para bromo complex, whereupon $\nu(^{15}N{=}^{14}N)$ occurred at 1399 cm^{-1}. Proton nmr spectra (saturated solution of para bromo complex in acetone-d_6) showed no evidence of metal hydride resonance in the range $\tau \pm 30$. Multiplet structure due to aromatic protons occurred at τ 2.46 from which individual resonance due to the 1,2,4-trisubstituted aromatic ring could not be distinguished. In addition a weak signal at τ 3.61 was observed having an integrated intensity corresponding to a single proton. This peak was split into a doublet at τ 3.46 and 3.75 in the ^{15}N-1 complex. It seems logical to ascribe this resonance, therefore, to the proton on N-1 of the arylazo function with $J(^{15}N\text{–}H) = 29$ Hz.

The presence of *o*-carbon coordination in the complex has been confirmed by a single-crystal X-ray study, the details of which will be published separately. **2** (X = F) crystallizes from acetone (incorporating one $(CH_3)_2CO$ molecule per asymmetric unit) in the orthorhombic space group $P2_12_12_1$: $M = 1047.9$, $a = 16.008$ (7), $b = 18.620$ (10), $c = 14.935$ (7) Å, $U = 4452$ Å^3, $d_m = 1.55$ (1), $d_c = 1.563$ g cm^{-3}, $Z = 4$, λ 0.70926 Å. The dimensions and esd's given in Figure 1 are appropriate to the present stage of refinement ($R = 0.032$) based upon 882 observed reflections in the range $0° < 2\theta < 30°$. The nonaromatic hydrogen atom in the complex has not been located with certainty; however, a comparison of possible models supports the presence of an N-1–H rather than an N-2–H bond.

Protonation of the terminal nitrogen atom of an arylazo group in the process of coordination to a transition metal now seems to be a recurring feature, but this is the first observation of this arising as a result of apparent proton transfer from an aromatic ring. Other examples are insertion into a metal hydride bond,[1,2] and migration from the methylene group of diazoacetic ester.[5,6] Conversely, the formation of metal–*o*-carbon bonds regularly occurs in the reactions of azo complexes, but the proton is not observed to be transferred to the azo function.[7]

Deprotonation of **2** occurs with OH^-, $CH_3CO_2^-$, or Et_3N to yield the pink neutral complex **3**, which may



3, X = F, Br

be reconverted to **2** with aqueous HBF_4. The ir spectrum of **3** contains no bands assignable as ν(N–H) or $\nu(BF_4^-)$; ν(CO) occurs at 2000 cm^{-1} and ν(N═N) at 1450 cm^{-1}. *Anal.* Calcd for **3** (X = Br): C, 53.44; H, 3.42; N, 2.90. Found: C, 53.41; H, 3.44; N, 2.73.

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(5) M. L. H. Green and J. R. Sanders, *Chem. Commun.*, 956 (1957).

(6) J. R. Knox and C. K. Prout, *Acta Crystallogr., Sect. B*, **25**, 1952 (1969).

(7) G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970).

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Bonding of Molecular Nitrogen in *trans*-Hydrido(dinitrogen)bis(phosphine)iron(II) Tetraphenylborate. A Mössbauer Study

Sir:

We have previously reported the preparation and some spectroscopic properties of cationic compounds of the general formula *trans*-$[MH(L)(depe)_2]^+BPh_4^-$ (M = Fe, Ru, Os; L = CO, p-MeO·C_6H_4·NC, Me_3CNC, $P(OPh)_3$, $P(OMe)_3$, N_2, PhCN, and MeCN).[1,2] Mössbauer center shifts[2] indicated that the σ donor plus π acceptor ability ($\sigma + \pi$) increased in the order MeCN < PhCN $\sim$ N_2 < $P(OPh)_3$ $\sim$ $P(OMe)_3$ < Me_3CNC < p-MeO·C_6H_4·NC < CO. Thus N_2 is a much weaker ($\sigma + \pi$) ligand than CO or RNC, but comparable to PhCN and slightly stronger than MeCN.

The variations in quadrupole splittings (Table I), which can also be related to bonding properties,[3] were not discussed previously because the signs of the quadrupole splittings were not known. The determination of the sign of one of these compounds (compound **2**) makes it possible to separate, at least qualitatively, the relative σ and π characteristics of N_2 relative to those of the other neutral ligands. The sign of the QS for the N_2 complex could not be determined directly by the magnetic field technique because of its very small QS. However, the sign can be safely assumed (*vide infra*) after the sign for one of these compounds is determined.

Table I. Room Temperature Quadrupole Splittings for *trans*-$[FeH(L)(depe)_2]^+BPh_4^-$ Complexes

No.	L	QS
1	CO	(−)1.00
2	p-$MeOC_6H_4NC$	−1.14
3	Me_3CNC	(−)1.13
4	$P(OMe)_3$	(−)0.90
5	$P(OPh)_3$	(−)0.72
6	N_2	(−)0.33
7	PhCN	(−)0.58
8	MeCN	(−)0.46

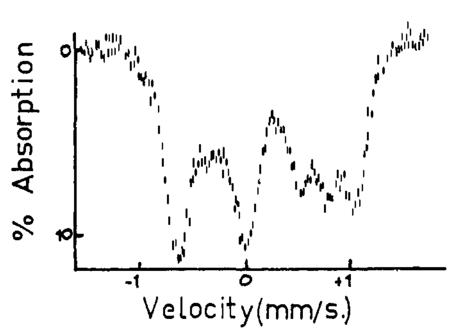

Figure 1. Mössbauer spectrum of compound **2** at 4°K in an applied magnetic field of 28 kG.

A typical spectrum of compound **2** in an applied longitudinal magnetic field of 28 kG at 4.2°K is shown in Figure 1. As discussed by Collins,[4] the two-line zero-field spectrum splits into a doublet and a triplet in a magnetic field. If the doublet is at positive velocities, the signs of V_{zz} and the quadrupole splitting are positive; if the doublet is at negative velocities, the sign of V_{zz} is negative. Figure 1 shows clearly that the doublet is at negative velocities, and the sign of V_{zz} is negative. This spectrum shows considerable deviation from that theoretically expected. This deviation is probably due either to preferred orientation effects or the Goldanskii–Karyagin effect.

The magnitude and sign of the quadrupole splitting for compound **2** is in good agreement with that expected from previously derived partial quadrupole splitting (PQS) values. Taking the PQS values of H^- to be −1.04, RNC = −0.69, and depe/2 = −0.62,[5] the predicted QS for compound **2** is −0.98 mm/sec compared with the observed −1.14 mm/sec. The predicted values for the phosphite compounds from derived PQS values[6] are also negative in sign, and the magnitudes are again in good agreement with the observed values. In addition, the range of PQS values observed for a large number of neutral ligands (−0.40 to −0.70)[6] gives an expected range of values for any *trans*-$FeHL(depe)_2^+$ species of −0.40 to −1.00 mm/sec. It is safe to assume then that all quadrupole splittings reported in Table I are negative.

The QS becomes more positive as the π acceptor function of L increases and more negative as the σ donor function of L increases, *i.e.*, QS $\propto (\pi - \sigma)$.[3] π acceptance withdraws d electron density along the Z EFG direction (from d_{XZ} and d_{YZ}), whereas σ donation increases the d electron density along the Z EFG direction (to d_{Z^2} and p_Z).

The molecular nitrogen compound has the most positive QS, indicating that it is the best ($\pi - \sigma$) ligand. By contrast, as noted earlier, the center shifts indicate that it is one of the poorest ($\sigma + \pi$) ligands. These results show that, relative to CO, N_2 is a much poorer ($\sigma + \pi$) ligand, but that π acceptance relative to σ donation is more important in N_2 than in CO. Or to compare N_2 with RCN ligands, the CS and QS data indicate that N_2 is a better π acceptor but a poorer σ donor than RCN. Relatively then, N_2 is a moderate π acceptor but a weak σ donor. This result is consistent with the conclusion presented previously[7] which

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(1) G. M. Bancroft, M. J. Mays, and B. E. Prater, *Chem. Commun.*, 585 (1969).

(2) G. M. Bancroft, M. J. Mays, B. E. Prater, and F. P. Stefanini, *J. Chem. Soc. A*, 2146 (1970).

(3) G. M. Bancroft, M. J. Mays, and B. E. Prater, *ibid.*, *A*, 956 (1970).

(4) R. L. Collins, *J. Chem. Phys.*, **42**, 1072 (1965).

(5) The signs of the QS chosen in ref 3 were incorrect [G. M. Bancroft, R. E. B. Garrod, A. G. Maddock, M. J. Mays, and B. E. Prater, *Chem. Commun.*, 200 (1970)] making the PQS values in Table II of ref 3 reversed about the value for Cl^-. The effect of the different signs is discussed.[3] The correct values for depe, H, and RNC[6] are obtained simply by inverting the values given in Table II about −0.30.

(6) G. M. Bancroft, R. E. B. Garrod, and A. G. Maddock, *J. Chem. Soc. A*, 3165 (1971); G. M. Bancroft and E. T. Libbey, unpublished observations.

(7) J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc. A*, 2841 (1969).