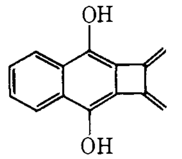
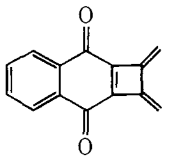
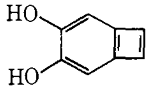


V

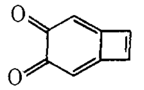


VI

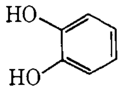
in the quinone instead of in the hydroquinone; this could happen in an appropriate orthoquinone. Indeed, Table I suggests that oxidation of VII to VIII should be easier than that of IX to X. The loss of ΔR upon oxidation is strongly diminished and the effect of the cyclobutadiene ring appears here in the HOMO of the hydroquinone which originates in the zero HOMO of the square cycle. Loss of electrons is thus facilitated in VII, and at the same time the electron-accepting tendency of the quinone produced is decreased (LEMO much more antibonding than in X).



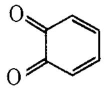
VII



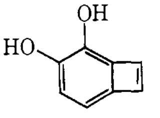
VIII



IX



X



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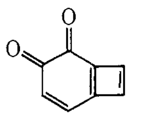
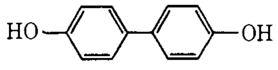
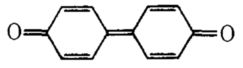


XII

In fact, the comparison of VII/VIII to XI/XII should be even more striking since the quinone XII shows the same effect as observed for II, namely a strong destabilization (ΔR = 1.21) and a bonding LEMO, which should tend to make the hydroquinone much more difficult to oxidize than VII.



XIII



XIV

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Received October 15, 1970

Crystal Structure of an Iridium–Tetrazene Complex Formed in the Reaction of Diazonium Salts with *trans*-Chlorocarbonylbis(triphenylphosphine)iridium(I)

Sir:

The reactions of aryldiazonium salts are receiving considerable attention at the present time, inasmuch as arylazo complexes of transition metals afford model systems for the bound nitrogen complex believed to be the initial step in atmospheric nitrogen fixation.[1,2] In all cases, it appears that the arylazo group binds to the metal through the unsubstituted nitrogen atom.[2–6]

As part of a systematic study of these complexes, we have carried out the reaction of several para-substituted phenyldiazonium tetrafluoroborate salts with Vaska's complex, *trans*-$IrCl(CO)(Ph_3P)_2$. The red crystals readily isolated from these reactions are now shown by a single-crystal X-ray structure analysis for the *p*-fluoro compound to consist of the iridium–1,4-*p*-fluorophenyltetrazene complex, $[Ir(N_4(C_6H_4F)_2)(CO)(Ph_3P)_2]BF_4\cdot C_6H_6$, rather than the closely related bisarylazo complex we at first expected to be present from chemical considerations. The possibility of the formation of tetrazene complexes in the reactions of aryldiazonium salts does not generally seem to have been recognized. Deeming and Shaw[5] reported the arylazo complex $[IrCl_2(PhN_2)(CO)(PhMe_2P)_2]$ from a similar synthesis in the presence of LiCl, and we are currently investigating other products in our reaction which we believe to be arylazo complexes.

In a typical preparation, a benzene–ethanol solution of $IrCl(CO)(Ph_3P)_2$ was treated at room temperature under argon with an equimolar quantity of the diazonium salt. Red, air-stable, diamagnetic crystals of the product were deposited from the deep red solution at 8°. *Anal.*[7] Calcd for $[Ir\{N_4(C_6H_4F)_2\}(CO)(Ph_3P)_2]BF_4\cdot C_6H_6$: C, 57.1; H, 3.81; N, 4.85; P, 5.36; F, 9.86. Found: C, 54.9; H, 3.80; N, 5.30; P, 5.10; F, 9.56. Conductivity measurements in nitromethane solution showed typical 1:1 electrolyte behavior (Λ_M = 100 ohm^{-1} cm^2 mol^{-1} at 1.5×10^{-4} *M*). The proton nmr spectra ($CDCl_3$ solution) showed multiplet peaks centered at τ 2.9 (triphenylphosphine and benzene) and 3.8 (*p*-fluorophenyl). ^{19}F nmr spectra in $CDCl_3$ solution (at 56.4 MHz using CAT) confirmed the presence of *p*-F (−6230 cps, weak) and BF_4^- (−8778 cps, strong) relative to a CCl_3F internal standard.[2] In the ir spectrum ν(CO) occurs at 2060 cm^{-1}, but we have been unable to detect bands due to nitrogen vibrations. Raman spectra are unavailable owing to decomposition in He–Ne laser radiation.

The compound crystallizes in the triclinic space group $P\bar{1}$; M = 1156, a = 13.669 (5), b = 17.423 (7), c = 10.852 (4) Å, α = 104.57 (3), β = 98.07 (5), γ = 88.43 (3)°, U = 2477 Å^3, D_m = 1.53 (3), Z = 2, λ 0.70926 Å, D_c = 1.549 g cm^{-3}. Intensities were measured using an automated Picker four-circle diffractometer and Mo Kα radiation (λ 0.7107 Å) up to 2θ = 45°. The structure was solved by Patterson and Fourier methods and refined by a full-matrix least-squares procedure. At present, R = 0.043 on 1396 independent reflections above background in the range 2θ 0–30°, with only the iridium atom allowed anisotropic thermal parameters. Further refinement, incorporating the remaining outer-sphere reflections, is continuing.

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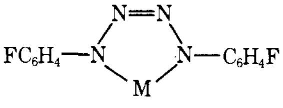
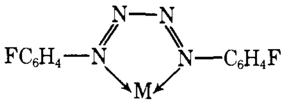
(7) Analyses were performed independently by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and A. Bernhardt, Munich. The C, N, and P results showed persistent and reproducible deviation, even after repeated recrystallization from benzene–acetone.

The structure of the complex cation is shown in Figure 1. The environment of Ir is quite irregular but may be viewed as based upon square-pyramidal geometry, having P(1) as the apex and atoms N(1), N(2), C(1), and P(2) at the base; these four atoms are not, however, coplanar. The present dimensions within the five-membered ring may be compared with representation **1** in which the iridium is σ bonded to the 1,4 positions of the tetrazene moiety, and representation **2** involving two-electron dative bonds from the 1,4 positions of a tetraazadiene group. Thus, the bond between N(3) and N(4) is significantly shorter than that between N(1) and N(3), and probably shorter than the N(2)–N(4) bond. The four nitrogen atoms are coplanar ($\chi^2 = 2.87$), with iridium displaced by only 0.12 Å out of this plane toward P(1). Atoms C(11) and C(21) of the phenyl groups are situated slightly above and below the plane, respectively. These features suggest that the structure is intermediate between representations **1** and **2**; however, because of the short central nitrogen–nitrogen bond we view the bonding as closer to **1**.



1



2

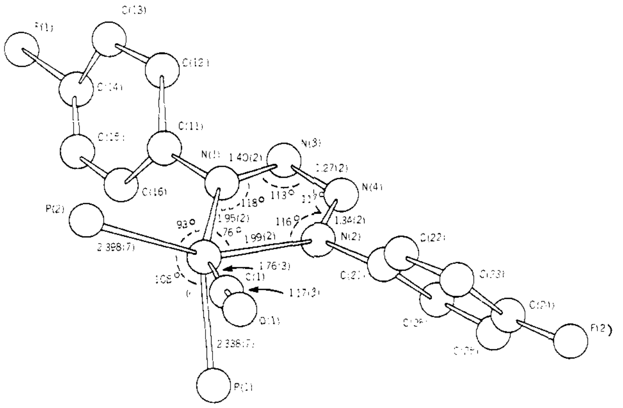


Figure 1. Molecular configuration of the complex ion $[Ir(N_4(C_6H_4F)_2)(CO)(Ph_3P)_2]^+$ (with esd's in the least significant figures in bond lengths in parentheses). Additional bond angles are C(1)IrN(1), 162; C(1)IrN(2), 94; C(1)IrP(1), 87; C(1)IrP(2), 90; N(1)IrP(1), 109; N(2)IrP(1), 98; N(2)IrP(2), 154; and IrC(1)O(1), 171°.

There are few other examples of complexes in which tetrazene-type ligands have been proposed.[8] A structure determination[9] on one of them, the complex $(Me_2N_4)Fe(CO)_3$, was interpreted in favor of representation **2**. A notable feature in that structure was short metal–nitrogen bonds, suggesting back-bonding from the iron atom to the tetraazadiene ligand. Delocalization of iridium 5d electrons into the π antibonding system of the nitrogen ligand does not appear to be a major factor in the Ir–N bonding in the present structure, since the mean observed bond length of 1.97 Å falls within the range (1.95–2.15 Å) proposed by Ibers and coworkers[10] for M–N single bonds, is close to the sum of Pauling single-bond covalent radii (2.02 Å), and is identical with the Ir–N bond length in the severely bent Ir–N–O group[11] in $[IrCl(NO)(CO)(Ph_3P)_2]BF_4$. The Ir–P(1) bond is significantly shorter than the Ir–P(2) bond. This may be due to a smaller π contribution to the Ir–P(2) bond, as might be expected to result from withdrawal of electrons from the iridium by the *p*-fluorophenyl groups. Ir–P bond lengths in the literature[11,12] show considerable variation with the number and type of ligands present and their disposition. It is difficult to draw exact comparisons, since to our knowledge this is the first example of a five-coordinate iridium complex containing phosphine ligands in both apical and basal positions; the values are, however, in agreement with other Ir–P bond lengths.[11]

We have yet to determine the mechanism for the formation of the complex. An attractive possibility is that the coordinated ligand arises *via* a mechanism which involves initial base attack of the Ir atom[11] on the substituted nitrogen atom of the phenylazo group, presumably functioning in the manner expected from the canonical structure $R—N^+≡N$. We are currently investigating this reaction further in an attempt to elucidate this mechanism.

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