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Catechol Oxidations. Characterization of Metal Complexes of 3,5-Di-*tert*-butyl-1,2-quinone 1-(2-Hydroxy-3,5-di-*tert*-butylphenyl)imine Formed by the Aerial Oxidation of 3,5-Di-*tert*-butylcatechol in the Presence of Ammonia and Divalent Metal Ions

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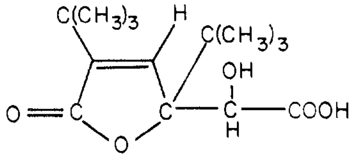
The aerial oxidation of 3,5-di-*tert*-butylcatechol in the presence of ammonia and divalent metal ions (Mg^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}) is shown to produce pseudooctahedral complexes which contain, as a tridentate ligand, the anion of 3,5-di-*tert*-butyl-1,2-quinone 1-(2-hydroxy-3,5-di-*tert*-butylphenyl)imine. The same complexes are formed by the reaction of the metal ion with 3,5-di-*tert*-butylcatechol, 3,5-di-*tert*-butyl-1,2-quinone, and ammonia in the absence of air. The analytically pure, crystalline complexes have been characterized by infrared, proton magnetic resonance, and electronic spectra. The electronic spectra are dominated by intense, ligand-based transitions which extend into the near-infrared region. The magnetic moments of the iron, nickel, and copper complexes are 5.33, 3.22, and 1.87 BM, respectively; the other complexes are diamagnetic. The electron spin resonance spectrum of the copper complex indicates that it possesses a tetragonally compressed ligand field with $g_\parallel < g_\perp$. A possible mechanism for the formation of the ligand is discussed.

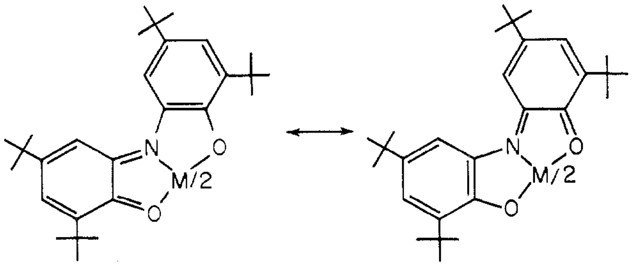
Introduction

The oxidation of 3,5-di-*tert*-butylcatechol has been studied under a variety of conditions. This particular catechol is particularly attractive for such studies since its pattern of substitution prevents many of the side and subsequent reactions which frequently accompany catechol oxidation. Under mildly basic conditions molecular oxygen will oxidize 3,5-di-*tert*-butylcatechol to 3,5-di-*tert*-butyl-1,2-quinone,[1] a relatively stable *o*-quinone. Transition metals have been shown to catalyze this reaction.[2,3] With an increase in alkalinity, the aerial oxidation of 3,5-di-*tert*-butylcatechol produces the lactone **1**. This product of ring opening apparently arises from attack of hydrogen peroxide on the quinone. This reaction has been of significance in considerations of the mechanism of action of the various catechol dioxygenases.[4,5]



1

During studies of the metal ion catalyzed oxidation of catechols, it was noted that deep green crystalline complexes were formed during the oxidation of 3,5-di-*tert*-butylcatechol when ammonia was present. The characterization of these complexes, which have been shown to have structure **2**, is the subject of this paper. This particular ligand, the anion of 3,5-di-*tert*-butyl-1,2-quinone 1-(2-hydroxy-3,5-di-*tert*-butylphenyl)imine, has been encountered once previously. The reaction of 2-amino-4,6-di-*tert*-butylphenol with arylthalium compounds also produces this ligand.[6]



2

Experimental Section

Preparation of Compounds. 3,5-Di-*tert*-butylcatechol was prepared by the published procedure.[7] The new metal complexes were all prepared by a common procedure which is outlined below for a typical example. A second method for the preparation of the zinc complex is also described.

$ZnC_{56}H_{80}N_2O_4$ from 3,5-Di-*tert*-butylcatechol and Oxygen. A solution of 5,24 g (24 mmol) of 3,5-di-*tert*-butylcatechol in 280 ml of 95% ethanol was added to a solution of 1.15 g (5.2 mmol) of zinc acetate dihydrate in 25 ml of water. After the addition of 20 ml of concentrated aqueous ammonia, a stream of air was gently bubbled through the solution. The solution rapidly became dark green and the presence of a dark green, crystalline solid became apparent after 20 min. After 3 hr of exposure to the air stream, the solution was filtered. The crystalline product was washed with water and ethanol and vacuum dried (yield 3.78 g, 80%). Purification was achieved by recrystallization from dichloromethane–ethanol.

$ZnC_{56}H_{80}N_2O_4$ from 3,5-Di-*tert*-butylcatechol and 3,5-Di-*tert*-butyl-1,2-benzoquinone. A solution of 0.44 g (2.0 mmol) of 3,5-*tert*-butylcatechol and 0.44 g (2.0 mmol) of 3,5-di-*tert*-butyl-1,2-benzoquinone was added to a solution of 0.22 g (1.0 mmol) of zinc acetate dihydrate in 10 ml of water. Immediately after the addition of 1 ml of concentrated aqueous ammonia to this mixture, the dark green crystalline product formed. The product was collected and purified as described above. The yield was 0.71 g (78%). This reaction does not appear to be affected by the presence of molecular oxygen; identical yields of the product are obtained regardless of whether or not oxygen is excluded from the system.

Physical Measurements. Molecular weights were measured by the use of a Mechrohm vapor pressure osmometer. Chloroform was the solvent and triphenylarsine was used as the standard. Magnetic susceptibilities were measured by the Gouy technique using powdered samples at ambient temperature (25 ± 1°). The magnetic standard was $HgCo(SCN)_4$. Infrared spectra were measured on a Perkin-Elmer 237 spectrophotometer with the sample suspended in mineral oil. Electronic spectra were recorded on a Cary 14 spectrophotometer. Proton magnetic resonance (^1H NMR) spectra for diamagnetic compounds were obtained by the use of a JEOL JNM-MH-100 spectrometer operating at 100 MHz. For paramagnetic compounds spectra were recorded using a JEOLCO PS-100 Digilab FTS operating at 100 MHz and 24°.

Results

The oxidation of 3,5-di-*tert*-butylcatechol with molecular oxygen in the presence of ammonia and a variety of divalent metal ions produces the metal complexes **2**. In solution these complexes are various shades of deep green; as solids they appear almost black. The complexes exhibit moderate solubility in chloroform, dichloromethane, hexane, and acetone. They are nearly insoluble in dimethylformamide, dimethyl

Table I. Analytical Data

Complex	% C		% H		% N		Mol wt	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found[a]
$MgC_{56}H_{80}N_2O_4$	77.35	77.42	9.27	9.40	3.22	3.11	869	867
$FeC_{56}H_{80}N_2O_4$	74.64	73.98	8.95	8.53	3.11	3.15	901	945
$NiC_{56}H_{80}N_2O_4$	74.41	74.65	8.92	8.79	3.10	3.08	903	909
$CuC_{56}H_{80}N_2O_4$	74.01	73.32	8.87	8.67	3.08	3.33	908	897
$ZnC_{56}H_{80}N_2O_4$	73.86	73.49	8.86	8.85	3.08	3.22	910	875
$CdC_{56}H_{80}N_2O_4$	70.24	69.95	8.42	8.22	2.92	2.73	957	922

[a] Measured in chloroform solution.

Table II. Infrared Spectra Data[a]

Compd	ν_{max}, cm^{-1}
$FeC_{56}H_{80}N_2O_4$	1515 s, 1372 s, 1360 s, 1344 w, 1319 sh, w, 1294 sh, s, 1281 vs, 1253 sh, m, 1288 m, 1222 m, 1194 sh, m, 1169 s, 1090 s, 1035 s, 1019 s, 994 m, 938 vw, 928 vw, 897 s, 850 w, 838 sh, w, 822 vw, 803 vw, 785 vw, 772 vw, 728 m
$NiC_{56}H_{80}N_2O_4$	1522 s, 1428 sh, vw, 1394 vw, 1375 s, 1362 s, 1347 s, 1294 vs, 1260 m, 1244 m, 1200 m, 1094 s, 1037 m, 1025 m, 1000 s, 944 vw, 928 vw, 900 s, 853 vw, 820 vw, 803 w, 794 w, 735 w
$CuC_{56}H_{80}N_2O_4$	1507 s, 1416 w, 1400 vw, 1375 s, 1360 s, 1347 s, 1304 vs, 1291 vs, 1260 s, 1241 sh, m, 1200 m, 1091 s, 1032 m, 1016 m, 1000 m, 953 vw, 925 vw, 897 s, 835 m, 822 vw, 800 w, 788 w, 728 w
$ZnC_{56}H_{80}N_2O_4$	1525 s, 1422 sh, vw, 1400 w, 1375 s, 1362 s, 1350 s, 1306 vs, 1262 m, 1244 sh, w, 1206 m, 1100 s, 1037 m, 1022 m, 1000 s, 956 vw, 930 vw, 900 s, 860 m, 837 vw, 825 vw, 803 w, 794 w, 735 w
$CdC_{56}H_{80}N_2O_4$	1522 s, 1410 vw, 1394 vw, 1372 s, 1360 s, 1344 s, 1290 vs, 1259 m, 1200 m, 1100 s, 1030 m, 1020 m, 995 s, 947 vw, 930 vw, 897 s, 853 m, 835 vw, 822 vw, 797 w, 789 w, 730 w
$MgC_{56}H_{80}N_2O_4$	1532 vs, 1425 w, 1394 s, 1372 s, 1360 s, 1344 s, 1294 vs, 1256 m, 1241 m, 1197 m, 1088 s, 1228 m, 1016 m, 991 s, 935 vw, 925 vw, 891 s, 850 w, 828 vw, 819 vw, 797 m, 791 m, 728 m

[a] Measured in Nujol mulls; absorbances in the region of strong Nujol absorption are not reported.

sulfoxide, and water. In acetone solution they are nonelectrolytes. The elemental analytical data and the molecular weight data set out in Table I are consistent with structure **2**.

The infrared spectra (Table II) of the various complexes **2** are nearly identical. The lack of absorptions in the regions associated with N–H and O–H stretching and bending vibrations is consistent with the absence of N–H and O–H units in these complexes. The spectra, especially the bands in the 1600–1500-cm^{-1} region, are consistent with the presence of a conjugated aromatic system.

The electronic spectrum of the zinc complex is reproduced in Figure 1 and the wavelengths of the absorption maxima of the complexes are reported in Table III. It is apparent that all of these spectra are similar. The extremely intense absorption at low energies is noteworthy. The intensity of these spectra suggests that electronic transitions within the ligands dominate the spectra. The similarity of the spectra of the various complexes indicates that a common ligand is present in each and strengthens the argument that the observed transitions are ligand based. The presence of these strong ligand absorptions renders the electronic spectra useless as diagnostic tools for probing the electronic structure of the metal ions.

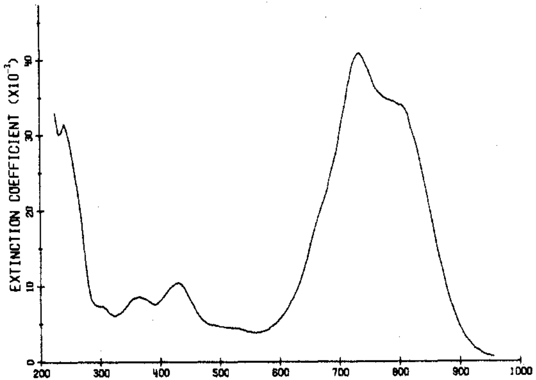


Figure 1. Electronic spectrum of $Zn(C_{28}H_{40}NO_2)_2$ in dichloromethane solution.

Table III. Electronic Spectra

Compd	λ_{max}, nm (ϵ)[a]
$MgC_{56}H_{80}N_2O_4$	793 (4.2 × 10^4), 725 (4.8 × 10^4), 655 sh (2.2 × 10^4), 525 (5.2 × 10^3), 436 (1.2 × 10^4), 358 (8.3 × 10^3), 340 (8.6 × 10^3), 305 (7.2 × 10^3)
$FeC_{56}H_{80}N_2O_4$	855 (1.8 × 10^4), 451 (1.5 × 10^4), 355 (1.9 × 10^4), 287 sh (2.1 × 10^4), 237 (3.8 × 10^4)
$NiC_{56}H_{80}N_2O_4$	837 (3.1 × 10^4), 768 (3.3 × 10^4), 475 sh (9.1 × 10^3), 432 (2.1 × 10^4), 409 sh (1.4 × 10^4), 303 sh (9.6 × 10^3), 236 (1.2 × 10^4)
$CuC_{56}H_{80}N_2O_4$	837 (2.5 × 10^4), 765 (3.0 × 10^4), 438 (1.3 × 10^4), 324 sh (9.4 × 10^3), 241 (3.5 × 10^4), 228 (3.4 × 10^4)
$ZnC_{56}H_{80}N_2O_4$	793 (3.5 × 10^4), 736 (4.0 × 10^4), 430 (1.0 × 10^4), 365 (8.7 × 10^3), 300 sh (7.2 × 10^3), 241 (3.1 × 10^4)
$CdC_{56}H_{80}N_2O_4$	815 (3.3 × 10^4), 743 (3.8 × 10^4), 535 sh (4.2 × 10^3), 428 (8.7 × 10^3), 305 sh (7.3 × 10^3), 265 (1.6 × 10^4)

[a] Measured in dichloromethane solution.

Table IV. Proton Magnetic Resonance Data[a]

Compd	Chem shifts	
	Ring protons	-C(CH$_3$)$_3$
$MgC_{56}H_{80}N_2O_4$	−7.40 (d), −7.20 (d)[b]	−1.26, −1.16
$FeC_{56}H_{80}N_2O_4$	−83.13 [184], −15.13 [150][d]	−3.20 [239], +2.11 [23][d]
$NiC_{56}H_{80}N_2O_4$	−29.45 [27],[d] −8.17 [163][d]	−0.21 [39], −1.76 [10][d]
$ZnC_{56}H_{80}N_2O_4$	−7.28 (d),[b] −7.12 (d)[b]	−1.23, −1.13
$CdC_{56}H_{80}N_2O_4$	−7.14	−1.22, −1.19
3,5-di-*tert*-butylcatechol[c]	−6.90 (d), −6.75 (d)[b]	−1.40, −1.24
3,5-di-*tert*-butylquinone	−6.93 (d), −6.20 (d)[b]	−1.23, −1.19

[a] In $CDCl_3$ solutions; ppm relative to TMS. [b] Doublets, $J_{H-C-C-H}$ = 2 Hz. [c] Chemical shift for -OH = −4.85 ppm. [d] Width in hertz at half-height given in brackets.

The ^{1}H NMR spectra of the complexes along with the spectra of 3,5-di-*tert*-butylcatechol and 3,5-di-*tert*-butyl-1,-2-benzoquinone are reported in Table IV. The spectra of the complexes are extremely similar. The spectra of the Mg(II), Zn(II), and Cd(II) complexes are indicative of diamagnetic species and consist of two singlets due to the *tert*-butyl groups and two doublets due to the aromatic protons. (In the cadmium complex the aromatic resonances appear to be accidentally degenerate.) The ^{1}H NMR spectrum of the zinc complex is invariant over the temperature range −70 to +20°. The ^{1}H NMR spectra of the iron and nickel complexes indicate the presence of paramagnetic metal ions. The resonances show sizable paramagnetic shifts and significant line broadening. A ^{1}H NMR spectrum of the copper complex could not be observed, presumably because of extreme line broadening which is characteristic of copper complexes with doublet ground states. The electron spin resonance spectrum of the copper complex was readily observed. At 20° in dichloromethane solution a broad resonance with $g = 2.132$ was observed. Under these conditions no hyperfine splittings were observed. At 20° a polycrystalline sample of the zinc complex doped with 1% of the copper complex exhibited an ESR spectrum which is characteristic of rhombic symmetry with $g_\perp = 2.226$ and $g_\parallel = 2.028$. Hyperfine structure in the region of $g_\parallel$ allowed the measurement of $A_\parallel(^{65,63}\text{Cu})$ as 100 G. The apparent hyperfine structure on the $g_\perp$ was not sufficiently resolved to allow $A_\perp$ to be measured.

The magnetic susceptibilities of polycrystalline samples of the copper, nickel, and iron complexes have been measured at 25 ± 1°. For the copper complex the magnetic moment was 1.87 BM; this is consistent with a doublet ground state and the observation of an electron spin resonance spectrum. The magnetic moments of the nickel and iron complexes are 3.22 and 5.33 BM, respectively.

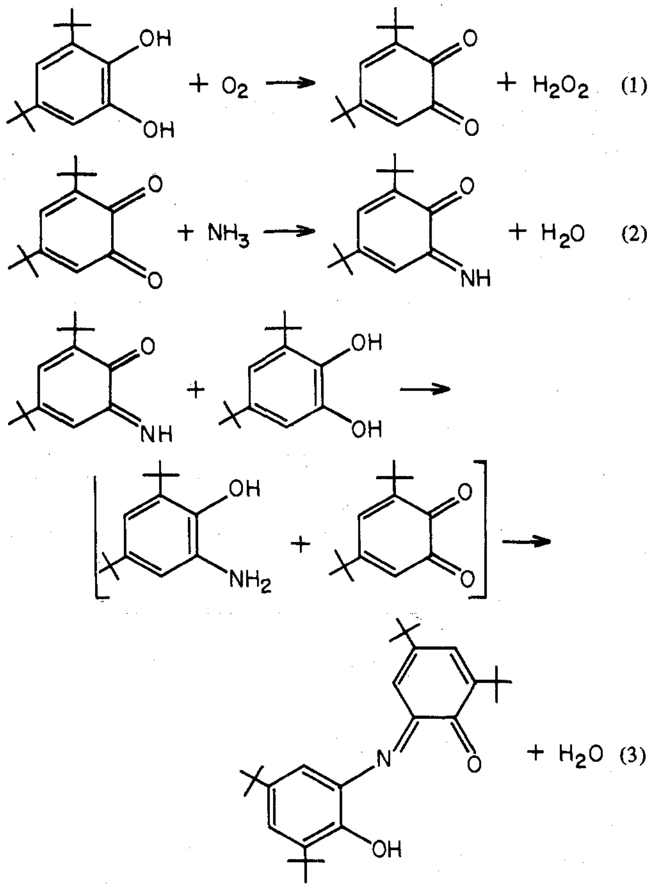
Discussion

From an examination of space–filling molecular models (Corey–Pauling–Koltum) we have concluded that only two types of polydentate coordination are possible for the ligand present in these complexes. One is the planar tridentate form shown in **2**. In this form, the ligand spans three meridional coordination sites. (The ligand is not capable of occupying three facial sites.) In the other possible geometry the ligand would function as a bidentate with the nitrogen and one of the oxygens acting as the donors. To achieve this mode of coordination, the phenyl ring attached to the noncoordinated oxygen would have to be rotated out of the M–N–O coordination plane. Although others[6] have proposed that this ligand might act as a bidentate ligand that would utilize two oxygen donors, inspection of models reveals that this is clearly impossible. The only arrangement in which both oxygen atoms can act as donors places these oxygens in trans positions and thereby forces the nitrogen atom to occupy the coordination site lying between these two trans oxygens. These models also indicate that the only reasonable pattern of *tert*-butyl substitution is that shown in **2**. For steric reasons this ligand could not accommodate *tert*-butyl substituents at either of the 6-phenyl ring positions.

We interpret the experimental results to indicate that, in all of the complexes reported here, the metal is coordinated by two similar tridentate ligands as indicated by **2**. Overall these complexes should have idealized D_{2d} symmetry. All of the complexes have similar electronic spectra. We anticipate that a fully conjugated, planar, tridentate ligand would have a different electronic spectrum than would a nonplanar bidentate ligand whose conjugation would be at least partially interrupted. Consequently, the similarities in electronic spectra of all of these complexes suggest that only one type of ligand geometry is present. The ^{1}H NMR spectra of all of the complexes indicate that all of the phenyl rings in each complex are symmetrically equivalent. This observation is consistent only with the ligand acting in a tridentate fashion. Considering the number of complexes examined and the variations in chemical shifts observed for these, it is unlikely that equivalence of phenyl resonances is caused by accidental degeneracies. The observation that the ^{1}H NMR spectrum of the zinc complex is invariant over a 90° temperature range indicates that the geometry of this complex is fairly fixed.

Although the electronic spectra are uninformative for characterization of metal–ligand bonding, the magnetic properties of the complexes do provide information about the ligand field properties of these tridentate chelates. The O_2N set of donors present in this ligand is expected to produce a weak ligand field. The observations described above suggest that the complexes are six-coordinate with some tetragonal distortion along the principal, N–M–N, axis. The magnetic susceptibility of the iron complex is consistent with the presence of a high-spin, six-coordinate d^6 ion and a weak ligand field. The magnetic susceptibility of the nickel complex (3.22 BM) is particularly diagnostic of the presence of six-coordination in this complex. Tetrahedral nickel complexes generally have magnetic moments greater than that observed for **2** (M = Ni), and planar nickel complexes are invariably diamagnetic. The copper complex exhibits magnetic properties characteristic of a doublet ground state. The electron spin resonance spectrum indicates the presence of tetragonal symmetry and is unusual since $g_\parallel < g_\perp$. The majority of tetragonally distorted, six-coordinate copper complexes have $g_\perp < g_\parallel$, a condition which is consistent with elongation or a weaker field along the tetragonal axis. The observation that $g_\parallel < g_\perp$ in **2** (M = Cu) indicates in this case that the axial field is stronger than the in-plane field[8] and that the odd electron principally occupies a d_{z^2} orbital which is probably directed along the N–Cu–N axis. This result is reasonable since nitrogen donors generally produce a stronger field than do oxygen donors. Additionally, inspection of models suggests that the metal–nitrogen distance may be compressed in order to allow for coordination by the two trans oxygen donors. It is significant to note, however, that the extent of this tetragonal distortion is not sufficient to reduce the spin multiplicities of either the nickel or iron complex. Other tetragonally compressed copper complexes are known. Jahn-Teller distortions take the form of tetragonal compression in salts of $Cu(NO_2)_6^{4-}$.[9,10] However, in the present case of **2** (M = Cu), the tetragonal compression is created by the ligand geometry. A similar situation occurs with the bis(diethylenetriamine)copper(II) cation. Again in this complex the two tridentate ligands occupy meridional coordination sites and produce, in the nitrate salt, a compressed tetragonal field which is reflected in both the X-ray structure[11] and the electron spin resonance[12] spectrum.

The facile formation of this unusual tridentate ligand requires comment. Although detailed mechanistic studies have not as yet been performed, the series of reactions 1–3 is presented as a plausible reaction pathway. The first step involves the oxidation of the catechol to the quinone by molecular oxygen. As indicated in the Introduction, this reaction is known to occur in alkaline solution. The second step involves the formation of a quinone imine; this type of condensation has been demonstrated previously.[13] The steric properties of the quinone ensure direction of this reaction so that only the indicated quinone imine is produced. In the last reaction, a redox reaction between the quinone imine and catechol produces the quinone and the aminophenol; these can then subsequently condense to form the desired Schiff base. As outlined, this scheme involves two-electron redox steps. Undoubtedly, some one-electron-transfer reactions do occur during this reaction, and radical coupling reactions may be



significant in the overall reaction, although they have not been specified.

The role of the various metal ions in this scheme has not been specified and in fact their role may be minimal. In the absence of a metal ion, the aerial oxidation of 3,5-di-*tert*-butylcatechol in the presence of ammonia produces a purple crystalline material which is as yet not fully characterized. It is not stable, especially in solution, and it appears from electron spin resonance and magnetic susceptibility measurements to contain a significant fraction of paramagnetic material.[14] Since this substance reacts with divalent metal ions to produce **2** in good yield, it appears that a precursor to **2** may be readily formed in the absence of metal ion.

We have verified that 3,5-di-*tert*-butyl-1,2-benzoquinone is an intermediate in the reaction and that the role of molecular oxygen is oxidation of 3,5-di-*tert*-butylcatechol to this quinone. The reaction of 3,5-di-*tert*-butyl-1,2-benzoquinone, 3,5-di-*tert*-butylcatechol, ammonia, and zinc acetate rapidly produces **2** (M = Zn) in good yield. Molecular oxygen has no discernible effect on this alternate mode of preparation of **2**.

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Registry No. $MgC_{56}H_{80}N_2O_4$, 56030-06-9; $FeC_{56}H_{80}N_2O_4$, 56030-07-0; $NiC_{56}H_{80}N_2O_4$, 56030-08-1; $CuC_{56}H_{80}N_2O_4$, 56030-09-2; $ZnC_{56}H_{80}N_2O_4$, 56030-10-5; $CdC_{56}H_{80}N_2O_4$, 56030-11-6; 3,5-di-*tert*-butylcatechol, 1020-31-1; ammonia, 7664-41-7; 3,5-di-*tert*-butyl-1,2-benzoquinone, 3383-21-9.

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Crystal and Molecular Structure of *trans*-Pentafluorophenylcarbonylbis(triphenylphosphine)iridium(I)

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The crystal structure of *trans*-pentafluorophenylcarbonylbis(triphenylphosphine)iridium(I), $C_6F_5[(C_6H_5)_3P]_2IrCO$, was determined by conventional Patterson, Fourier, and least-squares refinement techniques. The complex crystallizes in the monoclinic system, space group $P2_1/c$ with $a = 10.994$ (3) Å, $b = 13.459$ (2) Å, $c = 26.187$ (6) Å, $\beta = 108.49$ (3)°, and $Z = 4$. Intensity data (2145 reflections above background) were collected by the θ–2θ scan method out to $2\theta_{max} = 60°$ (Mo Kα) using a CAD-4 automated diffractometer. The final values of R_F and R_{wF} were 0.0394. Only the Ir atom, the atoms in its coordination sphere, and the carbon atoms of the pentafluorophenyl ring were refined anisotropically. The coordination about the iridium atom is slightly distorted square planar. The two phosphorus atoms are situated slightly above the best fit mean plane formed by the metal atom and the atoms bonded to it. Likewise the two carbon atoms in the coordination sphere are slightly below this plane. The iridium atom lies slightly above the line joining the two carbon atoms bonded to it but a little below the mean plane. Important bond distances are as follows: Ir–P, 2.305 (5) and 2.326 (4) Å; Ir–C(CO), 1.891 (17) Å; C–O, 1.137 (22) Å; Ir–C(C_6F_5), 2.090 (16) Å. The value of this latter bond indicates that extensive π overlap between the Ir atom and the pentafluorophenyl carbon atom, with consequent reduction of electron density of the metal atom, does not occur. Therefore, the reduced reactivity of the subject complex toward oxidative addition reactions must stem from other causes.

The report by Vaska and DiLuzio[2] in 1961 that the coordinatively unsaturated, planar d^8 complex chlorocarbonylbis(triphenylphosphine)iridium(I), I, could undergo various oxidative addition reactions with covalent molecules has