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**Intramolecular Conversion of a Five-Membered Iridacycle to a Three-Membered Counterpart by CO₂ Extrusion**

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**Abstract**
Thermolysis of the metallacycles 1a and 1b in refluxing toluene for 24 hours results in loss of CO₂ and the formation of a product characterized by the formal oxidative addition of the 16-electron Ir(I) metal fragment (CpIrPPh₃) into the nitrile triple bond, generating the kinetically very stable side-bonded nitrile complexes 2a and 2b, in high yield. An X-ray diffraction study was undertaken of 2a confirming its structure as that containing a Ir(III)-C=N metallacycle.
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Abstract

Thermolysis of the metallacycles 1a and 1b in refluxing toluene for 24 hours results in loss of CO\textsubscript{2} and the formation of a product characterized by the formal oxidative addition of the 16-electron Ir(I) metal fragment "CpIrPPh\textsubscript{3}\" into the nitrile triple bond, generating the kinetically very stable side-bonded nitrile complexes 2a and 2b, in high yield. An X-ray diffraction study was undertaken of 2a confirming its structure as that containing a Ir(III)-C=N metallacycle.
We have been investigating the reactivity of metallacycles generated by the cycloaddition of aryl nitrile oxides to low valent metal carbonyl complexes.\(^1\) We wish to report the formation of side-bonded nitrile complexes whose chemical characteristics appear to be more readily attributed to the result of oxidative addition across the nitrile triple bond by a metal fragment than by \(\sigma\)-complexation of a nitrile to a low valent metal.

Thermolysis of 1a and 1b \(^2\) in boiling toluene for 24 hours leads to the formation of the remarkably stable 2a and 2b, respectively, with extrusion of CO\(_2\). All \(^1\)H, \(^1\)\(^9\)F and \(^3\)\(^1\)P NMR data, as well as elemental analyses, are consistent with the structures shown for 2a and 2b.\(^3\) The structure of 2a was also confirmed by an X-ray diffraction study described below. The IR spectra of 2a and 2b exhibit

a CN stretching frequency at 1758 cm\(^{-1}\) and 1756 cm\(^{-1}\), respectively, a decrease of 472 cm\(^{-1}\) and 468 cm\(^{-1}\) from the corresponding free nitriles. Similar large decreases in the CN stretching frequencies have been observed in other complexes which are believed to contain side-bonded nitriles,\(^4\)\(^-\)\(^8\) as opposed to the more common mode of nitrile coordination which occurs by \(\sigma\)-bonding through the nitrile nitrogen lone electron pair.\(^9\) In order to establish whether the formation of free nitrile occurred by decomposition of 1, to generate the 16-electron metal fragment \(\text{CpIrPPh}_3\) which then coordinates free nitrile, or if an intramolecular mechanism was involved, 1b was decomposed in the presence of a 20-fold excess of \(p\)-ClC\(_6\)H\(_4\)CN. If nitrile formation occurred by the former mechanism, 2a would be the predominant product, whereas if an intramolecular process was involved, then compound 2b should be obtained. Both \(^3\)\(^1\)P and \(^1\)\(^9\)F NMR identified 2b as the predominant product (80% yield by NMR); no resonance in the \(^3\)\(^1\)P NMR was observed for 2a. This result indicated that no nitrile exchange had occurred and that the formation of 2 involved an intramolecular process. The \(^1\)\(^9\)F NMR of the products of decomposition of 1b gave two resonances, one of which corresponded to 2b and the other to free p-FC\(_6\)H\(_4\)CN. The yield of p-FC\(_6\)H\(_4\)CN was 9% by NMR in the absence of p-ClC\(_6\)H\(_4\)CN and 20% in the presence of p-ClC\(_6\)H\(_4\)CN; the \(^3\)\(^1\)P NMR contained a minor resonance at 17.09 ppm together with the major resonance due to 1b in both cases. The \(^1\)H NMR spectrum of the reaction products gave no evidence of hydrides which could be formed as
a result of C-H oxidative addition of the solvent or intramolecular hydride abstraction. The nature of the minor product resulting from loss of $P$-$FC_6H_4CN$ from 1b and having a $^{31}$P NMR resonance at 17.09 ppm was not determined.

The stability of 2a and 2b and their mode of formation strongly support a product which would result from formal oxidative addition of an Ir(I) 16-electron fragment to the CN triple bond thereby generating an Ir(III) Ir-C-N metallacycle, rather than simple $\pi$-complexation of a nitrile to a metal center. The nitrile ligands of 2a and 2b are not easily displaced. In contrast, the nitrile ligand of the side-bonded nitrile complex $(PPh_3)_2Pt(\pi-CF_3CN)$, is readily displaced by CO and diphenylacetylene at room temperature. The only side-bonded nitrile complexes comparable to 2a and 2b are molybdenocene nitrile complexes for which no crystallographic study is available to confirm their structure.

An X-ray diffraction study was undertaken of compound 2a, which established the nitrile ligand to be side-bonded to the Ir (Figure 1). The Ir-C(6) bond length is 2.11(2) Å, which is the expected length for an Ir(III)-C bond; the Ir-N bond distance is 2.17(2) Å which represents a long Ir-N single bond. The C(6)-N bond distance is 1.23(3) Å, which represents a lengthening of 0.08 Å to that of the free nitrile. No structural information is available to compare this C-N bond distance with other side-bonded nitrile complexes; a number of acetylene $\eta^2$ complexes have been structurally characterized and are observed to undergo large reductions in the C-C stretching frequencies and accompanying lengthening of the C-C bond. The average increase in the C-C bond length on coordination is 0.08 Å. The lengthening observed for the C-N distance of 2a is of the same magnitude, suggesting a similar reduction in the bond order.

From the intramolecular mode of formation of the nitrile complexes 2a and 2b, and their great chemical stability when compared to other side-bonded nitrile complexes, it appears that 2a and 2b are best described as formal Ir(III) metallacycles.

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**Supplementary Material Available:** Tables of positional and thermal parameters, interatomic distances and angles, and observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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We have synthesized a number of metallacycles by cycloaddition of aryl nitrile oxides with low valent metal carbonyl complexes. A preliminary communication has been published (Walker, J. A.; Knobler, C. B.; Hawthorne, M. F. J. Am. Chem. Soc. 1983 105, 3370.) and a complete report of this synthetic route to these metallacycles and their reactivity will be submitted shortly; the general reaction is outlined below. The metallacycle yields vary between 60 and 80%.

2. Selected data for 1a and 1b (full details will be reported elsewhere).  
1a: Anal. Calc. for C_{31}H_{24}ClIrNO_2P: C, 53.17; H, 3.46; Ir, 27.45; N, 2.00; P, 4.42. Found: C, 52.92; H, 3.57; Ir, 27.12; N, 1.91; P, 4.33. \(^1\)H NMR (CD_2Cl_2): 6 7.37-7.15 (complex multiplets, 19 H), 5.39 (d, 5 H, J = 1.0 Hz).  \(^{31}\)P(\(^1\)H) NMR (CD_2D_2): 6 -2.22.

1b: Anal. Calc. for C_{31}H_{24}FNO_2P: C, 54.37; H, 3.54; Ir, 28.07; N, 2.05; P, 4.52. Found: C, 54.12; H, 3.66; Ir, 27.92; N, 2.01; P, 4.44. \(^1\)H NMR (CD_2Cl_2): 6 7.46-6.74 (complex multiplets, 19 H), 5.393 (d, 5 H, J = 0.88 Hz).  \(^{31}\)P(\(^1\)H) NMR (CD_2D_2): 6 -2.09.

3. Selected data for 2a and 2b (full details will be reported elsewhere).  
2a: Anal. Calc. for C_{30}H_{24}ClIrNP: C, 54.83; H, 3.69; N, 2.13; P, 4.71. Found: C, 54.66; H, 3.60; N, 1.97; P, 4.08. \(^1\)H NMR (CD_6D_6): 6 7.15-8.24 (complex multiplets, 19 H), 5.90 (d, 5 H, J = 1.46 Hz).  \(^{31}\)P(\(^1\)H) NMR (CD_6D_5CD_3): 6 16.56.

2b: Anal. Calc. for C_{30}H_{24}FirNP: C, 56.23; H, 3.78; Ir, 29.99; N, 2.19; P, 4.83. Found: C, 55.70; H, 3.94; Ir, 29.42; N, 2.15; P, 4.71. \(^1\)H NMR (CD_2Cl_2): 6 4.67-6.82 (complex multiplets, 19 H), 5.267 (d, 5 H, J = 1.2 Hz).  \(^{31}\)P(\(^1\)H) NMR (CD_6D_5CD_3): 6 16.29.
10. Crystal data for 2a: \( \text{C}_{30}\text{H}_{24}\text{ClIrNP} \): \( M_r = 657.1 \); yellow-brown parallel-piped; orthorhombic; space group Pcn (standard setting, Pbcn); \( a = 10.638(2) \text{ Å}, b = 14.298(3) \text{ Å}, c = 33.310(5) \text{ Å}; V = 5066 \text{ Å}^3; Z = 8; D(\text{calc.}) = 1.72 \text{ g cm}^{-3} \). A total of 4254 unique reflections were collected of which 2495 were considered observed (\( I > 3\sigma(I) \)) and were used in subsequent calculations (Haiber diffractometer built by Professor C. E. Strouse of this department; \( \text{MoK}_\alpha \) radiation; graphite monochromator; \( \lambda = 0.7107 \text{ Å}; 0-2\theta \) scan; \( 0 < 2\theta < 54^\circ ; \mu = 5.733 \text{ cm}^{-1} \)). The structure was solved by the heavy atom method using SHELX 76. In the final least-squares cycle, based on \( F \), 307 parameters were refined including positional and anisotropic thermal parameters for one Ir, thirty C, one Cl, one N and one P. Refinement is currently at \( R = 0.077 \) and \( R_w = 0.086 \). The goodness of fit is 2.26.
Figure 1: ORTEP drawing of \([\text{C}_5\text{H}_5](\text{PPh}_3)\text{Ir}(\eta^2-\text{NCC}_6\text{H}_4\text{Cl})]\) (2a).

Hydrogen atoms have been omitted for clarity and phenyl groups are depicted schematically.
toluene, 110°C, 24hrs.

- CO₂

\[ \text{Ir} \quad x \quad \text{Ph}_3 \text{P} \]

1a, x = Cl  
1b, x = F

2a, x = Cl  
2b, x = F
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