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Registry No. **1a**, 18816-24-5; **1b**, 103530-75-2; **1c**, 1762-11-4; **3a**, 103457-11-0; **3b**, 103477-29-8; **3c**, 103457-12-1; **4a**, 103457-13-2; DMA, 781-43-1.

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(10) A control experiment showed that **3a** is photolabile under the conditions employed.

Intramolecular Conversion of a Five-Membered Iridacycle to a Three-Membered Counterpart by CO_2 Extrusion

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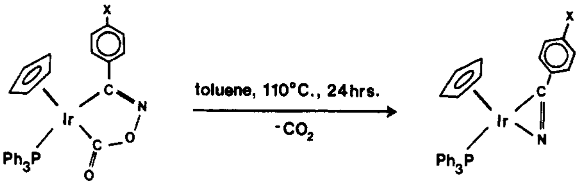
Summary: Thermolysis of the metallacycles **1a** and **1b** in refluxing toluene for 24 h results in loss of CO_2 and the formation of a product characterized by the formal oxidative addition of the 16-electron Ir(I) metal fragment "CpIrPPh$_3$" into the nitrile triple bond, generating the kinetically 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 $\overline{\mathrm{Ir^{III}{-}C{=}N}}$ 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 π-complexation of a nitrile to a low-valent metal.

Thermolysis of **1a** and **1b**[2] in boiling toluene for 24 h leads to the formation of the remarkably stable **2a** and **2b**, respectively, with extrusion of CO_2 (Scheme I). All ^{1}H, ^{19}F, and ^{31}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 and 1756 cm^{-1}, respectively, a decrease of 472 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 σ-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 "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 ^{31}P and ^{19}F NMR identified **2b** as the predominant product (80% yield by NMR); no resonance in the ^{31}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 ^{19}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 ^{31}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$_6$H$_4$CN from **1b** and having a ^{31}P NMR resonance at 17.09 ppm was not determined.

Scheme I



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

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

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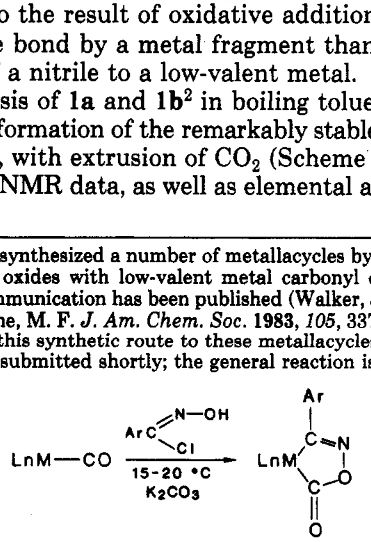
[1] We have synthesized a number of metallacycles by cycloaddition of aryl nitriles oxides with low-valent metal carbonyl complexes. A preliminary communication has been published (Walker, J. A.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1983**, *105*, 3370) and a complete report of this synthetic route to these metallacycles and their reactivity will be submitted shortly; the general reaction is outlined.



Ar = p-ClC$_6$H$_4$–, 2,4,6-(CH$_3$)$_3$C$_6$H$_2$–, and p-FC$_6$H$_4$–. Metallacycle yields vary between 60 and 80%.

[2] Selected data for **1a** and **1b** (full details will be reported elsewhere[1]). **1a**: ^{1}H NMR (CD$_2$Cl$_2$) δ 7.37–7.15 (complex multiplets, 19 H), 5.39 (d, 5 H, J = 1.0 Hz); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ −2.22. Anal. Calcd for C$_{31}$H$_{24}$ClIrNO$_2$P: 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. **1b**: ^{1}H NMR (CD$_2$Cl$_2$) δ 7.46–6.74 (complex multiplets, 19 H), 5.39 (d, 5 H, J = 0.88 Hz). ^{31}P{^{1}H} NMR (C$_1$D$_5$CD$_3$ δ −2.09. Anal. Calcd for C$_{31}$H$_{24}$FIrO$_2$P: 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.

[3] Selected data for **2a** and **2b** (full details will be reported elsewhere[1]). **2a**: ^{1}H NMR (C$_6$D$_6$) δ 7.15–6.24 (complex multiplets, 19 H), 5.90 (d, 5 H, J = 1.46 Hz); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 16.56. Anal. Calcd 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. **2b**: ^{1}H NMR (CD$_2$Cl$_2$) δ 7.67–6.82 (complex multiplets, 19 H), 5.27 (d, 5 H, J = 1.2 Hz); ^{31}P{^{1}H} NMR (C$_6$D$_5$CD$_3$) δ 16.29. Anal. Calcd 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.

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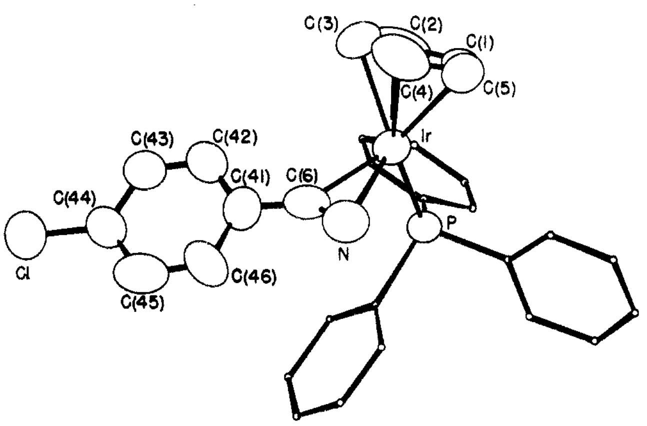

Figure 1. ORTEP drawing of [$(C_5H_5)(PPh_3)Ir(\eta^2\text{-}NCC_6H_4Cl)$] (**2a**). Hydrogen atoms have been omitted for clarity, and phenyl groups are depicted schematically.

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) $\overline{\mathrm{Ir{-}C{=}N}}$ metallacycle, rather than simple π-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 $(PPh_3)_2Pt(\pi\text{-}CF_3CN)$[8] 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[4] for which no crystallographic study is available to confirm their structure.

An X-ray diffraction study was undertaken of compound **2a**,[10] 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;[11,12] the Ir–N bond distance is 2.17 (2) Å which represents a long Ir–N single bond.[13,14] The C(6)–N bond distance is 1.23 (3) Å, which represents a lengthening of 0.08 Å relative 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 η^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.[14,15] 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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Registry No. 1a, 103731-57-3; 1b, 103731-58-4; 2a, 103731-59-5; 2b, 103751-00-4.

Supplementary Material Available: Figure 1s, packing diagram, Figure 2s, atom numbering scheme, and tables of positional and thermal parameters and interatomic distances and angles (9 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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[10] Crystal data for **2a**: $C_{30}H_{24}ClIrNP$: M_r 657.1; yellow-brown parallelpiped; orthorhombic; space group *Pcan* (standard setting, *Pbcn*); $a = 10.638$ (2) Å, $b = 14.298$ (3) Å, $c = 33.310$ (5) Å; $V = 5066$ Å^3; $Z = 8$; D(calcd) = 1.72 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 (Hüber diffractometer built by Professor C. E. Strouse of this department; Mo Kα radiation; graphite monochromator; $\lambda = 0.7107$ Å; θ–2θ scan; $0 < 2\theta < 54°$; $\mu = 5.733$ 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, 30 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.

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$HFe(CO)_4^-$, a Versatile Reagent toward Chlorophosphines. Facile Synthesis of New Phosphorus Transition-Metal Complexes

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Summary: Depending on the experimental conditions, reaction of $[Ph_4P][HFe(CO)_4]$ (**1**) with phenyldichlorophosphine leads quantitatively either to the stable secondary halophosphine complex $PhP(H)ClFe(CO)_4$ (**2b**), or to the first nonhindered side-on and end-on diphosphene complex $[Fe(CO)_4[\mu\text{-}Fe(CO)_4](PPh)_2]$ (**5**), or to the first trimetallic anionic diphosphane species $[Ph_4P][Fe(CO)_4]_3P_2Ph_2H]$ (**7**). X-ray diffraction study confirms the structure of **5**. Addition of $[Et_4N][HW(CO)_5]$ to the diphosphene complex **5** affords another mixed trimetallic anionic diphosphane compound $[Et_4N][[Fe(CO)_4]_2W(CO)_5P_2Ph_2H]$ (**8**).

Recently, a number of publications described the reactivity of carbonylmetalate dianions $Na_2[M_2(CO)_{10}]$ (M = Cr, Mo, or W) or $Na_2Fe(CO)_4$ with $RPCl_2$ leading to a variety of phosphinidene, $[(CO)_5M]_2PR$, or diphosphene complexes, $[(CO)_5M]_nRP{=}PR$ (n = 1 or 2), depending on the experimental conditions and the steric hindrance of R.[1,2]

To our knowledge, no similar work has been devoted to the reactivity of anionic hydridocarbonylmetalate $[PPh_4][HFe(CO)_4]$ (1) with dichlorophosphines. We have since begun to investigate this reaction, and in this paper we report (i) a simple one-step quantitative synthesis of stable secondary halophosphine complexes RP(H)ClFe-

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