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Synthesis of Metallacycles by 1,3-Dipolar Cycloaddition Reactions between Low-Valent Metal Carbonyls and Aryl Nitrile *N*-Oxides

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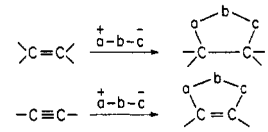
Reaction of low-valent metal carbonyl complexes with aryl nitrile *N*-oxides leads to the synthesis of novel five-membered metallacycles by 1,3-dipolar cycloaddition of the aryl nitrile *N*-oxide to the M–CO bond of the low-valent metal carbonyl complex. The syntheses of these metallacycles from metallacarborane carbonyl anions [*closo*-3-PPh$_3$-3-(CO)-3,1,2-MC$_2$B$_9$H$_{11}$]$^-$ (M = Ir, Rh) and [*closo*-2-PPh$_3$-2-(CO)-2,1,7-RhC$_2$B$_9$H$_{11}$]$^-$ and a number of pentamethylcyclopentadienyl and cyclopentadienyl complexes of Co, Rh, and Ir of the type (η^5-C$_5$R$_5$)LM(CO) (R = H, Me; L = PPh$_3$, PMe$_3$, CO) and the metal carbonyl anions M(CO)$_5^-$ (M = Mn, Re) are described. The syntheses of these metallacycles proceed in good yield (50–85%). The factors influencing the chemical and thermal stability of these metallacycles are discussed, and single-crystal X-ray diffraction studies of the metallacycles [PPN][*closo*-2-(PPh$_3$)-2-{η^2-C(*m*-FC$_6$H$_4$)-NOC(=O)-}-2,1,7-RhC$_2$B$_9$H$_{11}$] ([PPN]·**5b**) and (η^5-C$_5$Me$_5$)(PMe$_3$)Rh{η^2-C(*p*-FC$_6$H$_4$)NOC(=O)-} (**9**) are reported and their structures discussed. Crystallographic data for **9**: space group $P2_1/c$; a = 9.0376 (7) Å, b = 14.8675 (13) Å, c = 16.1965 (14) Å, β = 99.074 (3)°, V = 2149 Å^3, and Z = 4. For PPN·**5b**: space group $P\bar{1}$; a = 12.910 (5) Å, b = 13.270 (5) Å, c = 18.402 (7) Å, α = 88.24 (3)°, β = 109.46 (3)°, γ = 83.89 (3)°, V = 2948 Å^3, and Z = 2.

Introduction

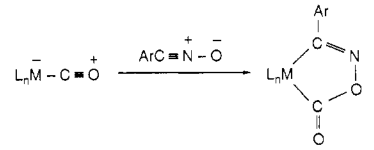
The study of the similarities of olefinic and acetylenic organic functions to certain organometallic species has developed into a significant area of contemporary chemistry. Indeed, the similarity in reactivity patterns of unsaturated organic species and certain organometallic functions has been formalized[1] in an isolobal relationship which include such organometallic species as (a) complexes which contain metal–metal multiple bonds (M=M or M≡M) (b) metal carbene and carbyne complexes (M=CR$_2$ or M≡CR), (c) low-valent metal complexes having carbonyl or isonitrile ligands in which π-back-bonding gives the M–CO and M–NCR bonds substantial multiple-bond character. In recent years, Stone[2] and co-workers have exploited the isolobal arguments of Hoffmann[1] in an extensive series of synthesis and structural studies of heteronuclear metal clusters. In these studies electronically and coodinatively unsaturated metal fragments were combined with class (a) and class (b) unsaturated organometallic species as defined above.

Although the multiple-bond character of the M–C bond in low-valent metal carbonyl and isonitrile complexes has long been recognized,[3] its reactivity as a unit has not received a great deal of attention. However, it occurred to us that the well-known 1,3-dipolar addition reagents, the aryl nitrile *N*-oxides, which effectively expanded organic heterocyclic chemistry by virtue of their cycloaddition reactions with carbon–carbon multiple bonds[4-6] (Scheme I) might undergo similar cycloaddition reactions with class (c) reagents (among others), the low-valent, coordinatively unsaturated metal carbonyls (Scheme II). The products of this sort of cycloaddition would be 4-metallaisoxazolin-5-one derivatives which would yield both CO$_2$ and aryl nitrile molecules upon decomposition of the metallacyclic ring. In addition, the metal center would have undergone a formal two-electron oxidation reaction. Such cycloaddition reactions proved to be very successful and were initially reported[7] in 1983. Later work which concerns the thermolysis of these new cyclometallic species has recently been communicated.[8]

Scheme I



Scheme II



In general, the investigation of the reactions of 1,3-dipolar reagents with transition metal complexes is limited and there are only a few examples of isolated products resulting from cycloaddition of dipolar reagents to M–C and M–M multiple bonds. Diazoalkanes react with dinuclear metal complexes containing metal–metal multiple bonds to form bridging diazoalkane and alkylidene products by addition of the diazoalkane across the metal–metal multiple bond;[9] for example, diazoalkanes show a wide

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[7] Walker, J. A.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1983**, *105*, 3370.

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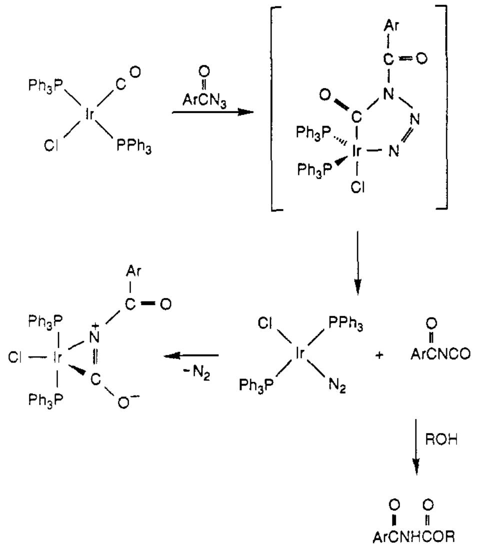
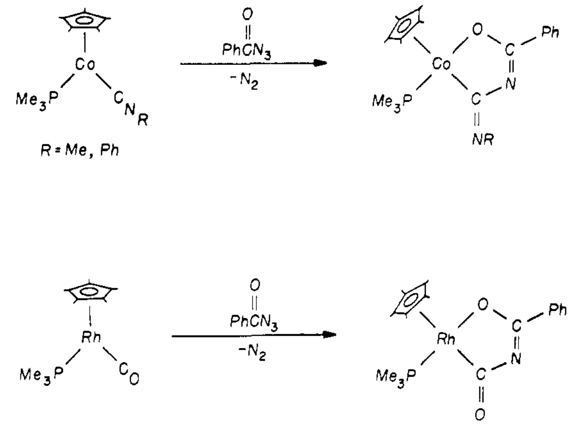
Scheme III

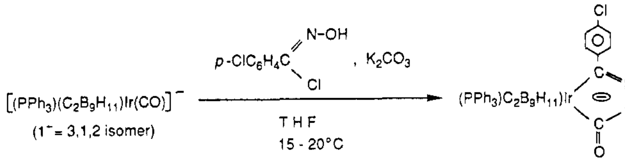


range of addition reactions across the Mo–Mo triple bond of $R_2Mo_2(CO)_4$ ($R = C_5H_5$, C_5H_4Me, C_5Me_5).[9a] Aryl azides show a similar reactivity with metal–metal multiple bonds.[10] These reactions are believed to proceed by initial cycloaddition of the 1,3-dipolar reagent to the metal–metal multiple bond to produce an intermediate cycloadduct which rapidly rearranges or loses N_2 to yield the observed products. Examples of the reactions of 1,3-dipolar reagents with low-valent metal carbonyl complexes are also limited in number; aroyl azides react with Vaska's complex *trans*-$(PPh_3)_2Ir(CO)Cl$ to produce the dinitrogen complex *trans*-$(PPh_3)_2Ir(N_2)Cl$ and an aroyl carbamate via an aroyl isocyanate in alcohol-containing solvents. In alcohol-free solvents the dinitrogen complex reacts with the aroyl isocyanate to form an aroyl isocyanate complex.[11] The mechanism originally proposed for the formation of the observed products was the 1,3-addition of the azide function to the Ir center to form a six-coordinate iridium complex which loses aroyl isocyanate to generate the dinitrogen complex. In view of the results reported in this paper, formation of the dinitrogen complex may occur by 1,3-dipolar addition of the aroyl azide to the Ir–CO bond of *trans*-$(PPh_3)_2Ir(CO)Cl$ to form a five-coordinate metallacycle which subsequently decomposes to yield the observed products (Scheme III). Similar reactions involving the conversion of organic azides and azide ion to isocyanates by metal carbonyl complexes[12] or by metal azide complexes in the presence of carbon monoxide have been reported.[12a,13] These reactions may very well proceed by the same general pathway as the reaction between aroyl azides and *trans*-$(PPh_3)_2Ir(CO)Cl$ proposed above.[11] In recent years metallacycles have been obtained by cycloaddition of isonitrile cobalt complexes with isocyanates and isothiocyanates,[14] and the reactions of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ with carbodiimides have been reported.[15] These reactions result from the cycloaddition of the organic functionality to the M–C bond of the isonitrile or carbonyl metal complexes. The reactions of the isonitrile complexes $(\eta^5\text{-}C_5H_5)(PMe_3)Co(CNR)$ (R = Me, Ph) and the metal carbonyl complex $(\eta^5\text{-}C_5H_5)(PMe_3)Rh(CO)$ with benzoyl azide lead to the formation of the metallacycles $(\eta^5\text{-}C_5H_5)(PMe_3)Co\{\eta^2\text{-}OC(Ph)NC(O)\text{-}\}$[16] and $(\eta^5\text{-}C_5H_5)(PMe_3)Rh\{\eta^2\text{-}OC(Ph)NC(O)\text{-}\}$[17] by cycloaddition to the Co–CNR and Rh–CO bonds, respectively (Scheme IV). Cycloaddition to the Co–CO of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ has also been observed in the photochemical reaction of this complex with dialkyl diazomalonates[18] while [3 + 2] cycloaddition by the bis(alkoxycarbonyl)carbene, $:C(CO_2R)_2$ ($R = CH_3$, C_2H_5), to $(C_5H_5)Co(CO)_2$ yields a five-membered metallacycle. These reactions clearly demonstrate the incipient reactivity of the M–C bond of low-valent metal carbonyl and metal isonitrile complexes.

Scheme IV



Scheme V



Results and Discussion

In considering a particular metal carbonyl complex as a possible substrate for cycloaddition with aryl nitrile *N*-oxides, two stereoelectronic features were sought. Firstly, an electron-rich metal center was necessary in order

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(9) (a) Curtis, M. D.; Messerle, L.; D'Errico, J. J.; Butler, W. M.; Hay, M. S. *Organometallics* **1986**, *5*, 2283. (b) Messerle, L.; Curtis, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 7789. (c) Clauss, A. D.; Dimas, P. A.; Shapley, J. R. *J. Organomet. Chem.* **1980**, *201*, C31. (d) Boag, N. M.; Green, M.; Mills, R. N.; Pain, G. N.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1980**, 1171. (e) Green, M.; Mills, R. N.; Geoffrey, N. P.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 1309. (f) Herrmann, W. A.; Bauer, C.; Plank, J.; Kalcher, W.; Speth, D.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 193. (g) D'Errico, J. J.; Messerle, L.; Curtis, M. D. *Inorg. Chem.* **1983**, *22*, 849. (h) Herrmann, W. A.; Bauer, C. *J. Organomet. Chem.* **1981**, *204*, C21. (i) Bell, L. K.; Herrmann, W. A. *J. Organomet. Chem.* **1982**, *239*, C4. (j) Bell, L. K.; Herrmann, W. A.; Kriechbaum, G. W.; Pfisterer, H.; Ziegler, M. L. *J. Organomet. Chem.* **1982**, *240*, 381.

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to ensure sufficient nucleophilicity for reaction with the carbon atom of the nitrile *N*-oxide function. It was also important that a metal complex was selected in which the metal center was capable of expanding its coordination number from four to five or from five to six. A number of five-coordinate half-sandwich metal carbonyl complexes of Co, Rh and Ir are known which have η^5-cyclopentadienyl anion[19a] or η^5-dicarbollide dianion ligands[19b,c] coordinated to the basic metal center. At the outset of this research, the closo metallacarborane anions $[(PPh_3)(C_2B_9H_{11})M(CO)]^-$ (M = Ir, Rh)[19b,c] had been recently synthesized in our laboratories and were recognized as having the desired structural and electronic features thought to be required for 1,3-dipolar cycloaddition reactions with aryl nitrile *N*-oxides. Consequently, these species provided the first successful examples of the new cycloaddition reaction.[7]

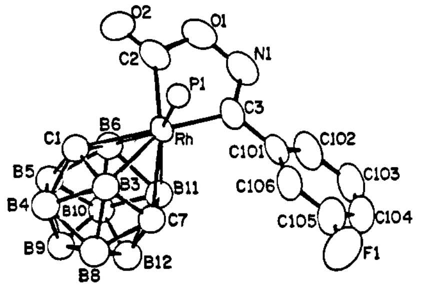

Figure 1. ORTEP projection of the anion of [PPN][*closo*-2-(PPh_3)-2{η^2-C(m-FC_6H_4)NOC(=O)-}-2,1,7-$RhC_2B_9H_{11}$ (PPN·**5b**). Hydrogen atoms have been omitted for clarity.

Table I. Selected Distances and Angles

9		PPN·5b	
	Distances (Å)		
Rh–C(14)	2.021 (5)	Rh–C(3)	2.016 (7)
Rh–C(15)	1.998 (5)	Rh–C(2)	1.989 (8)
Rh–C(1)	2.230 (4)	Rh–C(1)	2.282 (7)
Rh–C(2)	2.259 (4)	Rh–C(7)	2.330 (7)
Rh–C(3)	2.295 (4)	Rh–B(3)	2.234 (9)
Rh–C(4)	2.289 (4)	Rh–B(6)	2.232 (9)
Rh–C(5)	2.249 (4)	Rh–B(11)	2.260 (9)
Rh–P	2.268 (1)	Rh–P(1)	2.346 (2)
C(15)–O(2)	1.399 (6)	C(2)–O(1)	1.390 (9)
O(2)–N	1.427 (6)	O(1)–N(1)	1.426 (8)
C(14)–N	1.279 (7)	C(3)–N(1)	1.273 (9)
C(15)–O(1)	1.200 (7)	C(2)–O(2)	1.198 (9)
C(14)–C(16)	1.498 (6)	C(3)–C(101)	1.476 (10)
	Angles (deg)		
P–Rh–C(14)	91.0(1)	P–Rh–C(3)	93.3 (2)
P–Rh–C(15)	86.9 (1)	P–Rh–C(2)	85.4 (2)
P–Rh–C(1)	160.5 (1)	P–Rh–B(6)	152.5 (2)
P–Rh–C(2)	139.9 (1)	P–Rh–B(11)	152.8 (2)
P–Rh–C(3)	107.0 (1)	P–Rh–C(7)	112.6 (2)
P–Rh–C(4)	99.9 (1)	P–Rh–B(3)	90.9 (2)
P–Rh–C(5)	124.7 (1)	P–Rh–C(1)	111.3 (2)
C(15)–Rh–C(14)	77.4 (3)	C(2)–Rh–C(3)	77.8 (3)
Rh–C(15)–O(1)	130.0 (4)	Rh–C(2)–O(2)	130.2 (6)
O(1)–C(15)–O(2)	114.9 (5)	O(2)–C(2)–O(1)	116.0 (7)
Rh–C(15)–O(2)	115.0 (3)	Rh–C(2)–O(1)	113.7 (6)
C(15)–O(2)–N	114.2 (4)	C(2)–O(1)–N(1)	116.4 (6)
O(2)–N–C(14)	113.5 (4)	O(1)–N(1)–C(3)	111.6 (6)
Rh–C(14)–N	119.6 (4)	Rh–C(3)–N(1)	120.4 (6)
Rh–C(14)–C(16)	126.8 (3)	Rh–C(3)–C(101)	120.4 (6)
N–C(14)–C(16)	113.6 (4)	N(1)–C(3)–C(101)	112.3 (7)

Synthesis of Metallacycles from Metallacarborane Complexes. A THF solution of *p*-chlorobenzohydroxamic acid chloride was added over a period of 3 h to a THF solution of the PPN$^+$ salt of the iridacarborane anion [*closo*-3-(PPh_3)-3-(CO)-3,1,2-$IrC_2B_9H_{11}$]$^-$ (PPN·**1**) maintained at 15–20 °C in the presence of K_2CO_3.[20] The yellow solution of the starting anion became paler in color as the reaction proceeded. Filtration followed by addition of pentane produced a pale yellow solid, which on recrystallization from THF–ether yielded analytically pure crystals, which were spectroscopically characterized as the metallacycle [PPN][*closo*-3-(PPh_3)-3-{η^2-C(*p*-ClC_6H_4)-NOC(=O)-}-3,1,2-$IrC_2B_9H_{11}$)] (PPN·**2**) (Scheme V). The metallacycle results from the cycloaddition of the *p*-chlorobenzonitrile *N*-oxide generated in situ to the Ir–CO bond. Slow addition of the *p*-chlorobenzohydroxamic acid chloride was necessary to prevent the intermediate arylnitrile *N*-oxide from dimerizing to form 1,2,5-oxadiazole 1-oxides (furoxans).[4–6] This spontaneous dimerization was further inhibited by maintaining a low reaction temperature. The reaction could be conveniently monitored by IR spectroscopy of the reactants and products in solution by observing the growth of the 1650 cm^{-1} absorption due to the exocyclic C=O and the simultaneous decrease in the intensity of the absorption at 1903 cm^{-1} due to the starting carbonyl anion. The analogous rhodacarborane anions [*closo*-3-(PPh_3)-3-(CO)-3,1,2-$RhC_2B_9H_{11}$]$^-$ (**3a**$^-$) and [*closo*-2-(PPh_3)-2-(CO-2,1,7-$RhC_2B_9H_{11}$]$^-$ (**3b**$^-$)[7] displayed similar reactivities. Dichloromethane solutions of the [Et_4N^+] salts of **3a**$^-$ and **3b**$^-$ were reacted with benzohydroxamic acid chloride or *m*-fluorobenzohydroxamic acid chloride in the presence of K_2CO_3. After separation of K_2CO_3 from the reaction mixture and recrystallization, analytically pure yellow-white solids were obtained of the tetraethylammonium salts of the metallacycles [Et_4N]-[*closo*-3-(PPh_3)-3{η^2-C(C_6H_5)NOC(=O)-}-3,1,2-$RhC_2B_9H_{11}$] (Et_4N·**4a**), [Et_4N][*closo*-3-(PPh_3)-3-{η^2-C(*m*-FC_6H_4)NOC-(=O)-}-3,1,2-$RhC_2B_9H_{11}$] (Et_4N·**5a**) and [Et_4N][*closo*-2-(PPh_3)-2-{η^2-C(*m*-FC_6H_4)(=O)-}-2,1,7-$RhC_2B_9H_{11}$] (Et_4N·**5b**), formed by cycloaddition of the aryl nitrile *N*-oxide to the Rh–CO bond. All the metallacycles obtained displayed a characteristic strong infrared spectra absorption between 1700 and 1640 cm^{-1} due to the exocyclic C=O and medium to weak absorption between 1540 and 1520 cm^{-1} in the C=N region.

X-ray Crystal Structure of [PPN][*closo*-2-(PPh_3)-2-{η^2-C(*m*-FC_6H_4)NOC(=O)-}-2,1,7-$RhC_2B_9H_{11}$] (PPN·5b). In order to unequivocally establish the structure of these metallacycles, a single-crystal X-ray diffraction study of the [PPN$^+$] salt of **5b**$^-$ was undertaken. The ORTEP projection of the anion is shown in Figure 1 and reveals the expected structure of the five-membered metallacycle. Table I lists selected interatomic bond distances and bond angles while positional and vibrational parameters are listed in Table II. The structure is that of the expected cycloadduct formed by cycloaddition of the *m*-fluorobenzonitrile *N*-oxide to the Rh–CO bond. The Rh center exhibits pseudooctahedral coordination, and its coordination number increases from five to six as the Rh(I) is formally oxidized to Rh(III) during cycloaddition. Three of the coordination sites are formally occupied by the η^5-7,9-dicarbollide ligand, one site is occupied by triphenyl phosphine, and the remaining two sites are occupied by the two carbon atoms of the η^2-chelate ligand. Two fea-

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(20) The nitrile *N*-oxides are generated in situ from their hydroxamic acid chlorides; treatment of hydroxamic acid chloride with K_2CO_3 results in the elimination of HCl to produce the nitrile oxide.

$$ArC(=N-OH)Cl \xrightarrow[THF]{K_2CO_3} ArC\equiv\overset{+}{N}-\overset{-}{O}$$

Table II. Positional and Vibrational Parameters for Non-Hydrogen Atoms in PPN•5b and 9

PPN·5b[a]

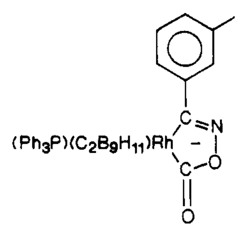
atom	*x*	*y*	*z*	*B*(equiv), Å^2
Rh(2)	0.37743 (4)	0.19294 (4)	0.25646 (3)	2.9
P(1)	0.2211 (1)	0.1056 (1)	0.2224 (1)	3.0
O(1)	0.2739 (5)	0.3241 (5)	0.1201 (3)	6.0
N(1)	0.2495 (5)	0.3800 (5)	0.1786 (4)	5.5
F	0.1918 (5)	0.3555 (5)	0.4759 (4)	9.4
C(102)	0.2739 (7)	0.4926 (7)	0.3077 (6)	5.7
C(103)	0.2515 (8)	0.5508 (8)	0.3631 (7)	6.8
C(104)	0.2231 (8)	0.5051 (9)	0.4190 (8)	6.9
C(105)	0.2190 (7)	0.4026 (8)	0.4190 (6)	5.9
C(106)	0.2400 (6)	0.3442 (7)	0.3640 (6)	5.0
C(101)	0.2672 (5)	0.3885 (6)	0.3060 (5)	4.1
O(2)	0.3557 (5)	0.1826 (5)	0.0944 (3)	5.9
C(2)	0.3351 (6)	0.2290 (6)	0.1438 (5)	4.4
C(3)	0.2869 (5)	0.3298 (5)	0.2440 (5)	4.0
N(2)	0.3042 (4)	0.2767 (4)	0.7752 (3)	3.1 (1)
P(2)	0.1976 (1)	0.2385 (1)	0.7845 (1)	2.99 (3)
P(3)	0.3516 (1)	0.3788 (1)	0.7642 (1)	2.95 (4)
C(1)	0.5333 (6)	0.0879 (6)	0.2643 (4)	4.1 (2)
B(3)	0.4799 (7)	0.0598 (7)	0.3338 (5)	3.8 (2)
B(4)	0.6217 (8)	0.0189 (8)	0.3432 (6)	4.6 (2)
B(5)	0.6640 (8)	0.1171 (7)	0.2979 (6)	4.6 (2)
B(6)	0.5484 (7)	0.2136 (7)	0.2602 (5)	4.1 (2)
C(7)	0.4851 (6)	0.1624 (6)	0.3865 (4)	4.1 (2)
B(8)	0.5908 (8)	0.0660 (8)	0.4227 (6)	5.1 (2)
B(9)	0.7029 (8)	0.1057 (7)	0.3985 (5)	4.1 (2)
B(10)	0.6565 (7)	0.2269 (7)	0.3482 (5)	4.1 (2)
B(11)	0.5154 (8)	0.2626 (7)	0.3427 (5)	4.4 (2)
B(12)	0.6161 (8)	0.1935 (8)	0.4269 (6)	5.0 (2)

9[b]

atom	*x*	*y*	*z*	*U*^{2}, Å^2
Rh	0.32552 (3)	0.04123 (2)	0.21367 (2)	0.037
P	0.3815 (2)	0.1361 (1)	0.1133 (1)	0.053
F	0.9730 (4)	0.1812 (3)	0.4819 (2)	0.116
O(1)	0.2620 (4)	−0.0917 (3)	0.0802 (2)	0.074
O(2)	0.4915 (4)	−0.1003 (3)	0.1481 (3)	0.073
N	0.5975 (5)	−0.0585 (3)	0.2111 (3)	0.066
C(1)	0.1946 (4)	−0.0309 (2)	0.2290 (3)	0.065
C(2)	0.2605 (4)	0.0456 (2)	0.3427 (3)	0.066
C(3)	0.1987 (4)	0.1236 (2)	0.2998 (3)	0.060
C(4)	0.0947 (4)	0.0954 (2)	0.2297 (3)	0.061
C(5)	0.0921 (4)	−0.0001 (2)	0.2291 (3)	0.065
C(6)	0.2149 (13)	−0.1257 (5)	0.3249 (8)	0.149
C(7)	0.3583 (9)	0.0438 (8)	0.4252 (4)	0.141
C(8)	0.2200 (11)	0.2189 (5)	0.3297 (7)	0.130
C(9)	−0.0099 (9)	0.1548 (8)	0.1733 (6)	0.134
C(10)	−0.0153 (9)	−0.0561 (7)	0.1685 (6)	0.133
C(11)	0.5656 (7)	0.1264 (5)	0.0848 (4)	0.086
C(12)	0.3673 (9)	0.2561 (4)	0.1329 (4)	0.094
C(13)	0.2582 (8)	0.1224 (5)	0.0144 (3)	0.086
C(14)	0.5440 (5)	0.0085 (3)	0.2461 (3)	0.049
C(15)	0.3507 (6)	−0.0591 (3)	0.1349 (3)	0.052
C(16)	0.6564 (4)	0.0541 (2)	0.3105 (2)	0.051
C(17)	0.7850 (4)	0.0081 (2)	0.3465 (2)	0.062
C(18)	0.8925 (4)	0.0514 (2)	0.4042 (2)	0.076
C(19)	0.8714 (4)	0.1408 (2)	0.4259 (2)	0.075
C(20)	0.7427 (4)	0.1868 (2)	0.3899 (2)	0.073
C(21)	0.6353 (4)	0.1435 (2)	0.3322 (2)	0.061

[a] Parameters for rigid groups are included with supplementary material. Esd's for vibration parameters are given only for atoms refined isotropically. Anisotropic parameters for other atoms are included with supplementary material. [b] Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. Isotropic values are [$1/(8\pi^2)$] times the "equivalent *B* value" for an anisotropic atom, as defined by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609–610.

tures of interest are that the five-membered metallacycle is essentially planar and that the Rh–C(2) bond length, 1.989 (8) Å, and the Rh–C(3) bond length, 2.016 (7) Å, are very short when compared to other reported rhodium–alkyl σ bonds.[21] These values are comparable to the lengths of Rh–C bonds which are strengthened by metal to ligand π-back-bonding.[22] For example, the Rh–C bond length of the carbene chelate complex $I_3(CO)RhCPh(NMe)CPhNMe$[22c] is 1.97 Å and that of the rhodium complex (η^5-C_5Me_5)(PMe_3)Rh(C_6H_5)Br[22d] is 2.05 Å. This suggests that substantial π-back-bonding occurs from the Rh(III) center to delocalized π^* acceptor orbitals of the cyclic ligand. The bond lengths within the metallacycle itself are in agreement with the valence bond representation shown below, which may be identified as a 4-rhodaisoxazolin-5-one.



Synthesis of Metallacycles from Pentamethylcyclopentadienyl and Cyclopentadienyl Metal Carbonyl Complexes. Cyclopentadienyl and pentamethylcyclopentadienyl metal carbonyl complexes of cobalt, rhodium, and iridium also react with aryl nitrile *N*-oxides to form cycloadducts. When a THF solution of (η^5-C_5Me_5)Ir$(CO)_2$ and mesitylene nitrile *N*-oxide was stirred at room temperature for 8 h, the yellow solution became colorless. Addition of pentane produced the analytically pure metallacycle (η^5-C_5Me_5)(CO)Ir{η^2-C(2,4,6-$Me_3C_6H_2$)-NOC(═O)-} (**6**) in 65% yield. A number of metallacycles have been generated by the cycloaddition of aryl nitrile *N*-oxides with pentamethylcyclopentadienyl and cyclopentadienyl metal carbonyl complexes, such as (η^5-C_5Me_5)(PMe_3)Rh(CO), (η^5-C_5Me_5)Rh$(CO)_2$, and (η^5-C_5Me_5)(PPh_3)M(CO) (M = Ir, Rh, Co) (Table III). The ^{1}H NMR of **6** reveals that the three methyl groups on the exocyclic mesityl group are inequivalent, indicating that the mesityl group does not rotate rapidly about the C–C bond. This restricted rotation is undoubtedly due to steric hindrance, since free rotation is observed in the case of complex **7** wherein the *p*-chlorobenzyl group is less sterically demanding. When the reaction is carried out at a higher temperature (30 °C), the metallacycle **6** is formed more rapidly. However, under these conditions **6** is thermally labile and some decomposition occurs with the release of 2,4,6-trimethylbenzonitrile, identified by the C–N stretch in the infrared spectrum of the products. The use of aryl nitrile *N*-oxides with sterically bulky substituents such as mesitylene nitrile *N*-oxide is convenient as these nitrile *N*-oxides do not dimerize spontaneously in solution[23] and are not required to be generated in situ. The steric bulk of these 1,3-dipolar reagents, however, makes them less reactive. As an example, mesitylene nitrile *N*-oxide does not react with the iridacarborane anion [*closo*-3-(PPh_3)-3-(CO)-3,1,2-$IrC_2B_9H_{11}$]$^-$ (1^-) although the less sterically bulky *p*-chlorobenzonitrile *N*-oxide did react to produce cycloadduct 2^-. Solutions of **6**, and of other

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Table III. Yield, Melting Point, and Exocyclic C=O Stretching Frequencies of Metallacycles Synthesized

compound	yield, %	mp,[a] °C	ν(C=O), cm^{-1}
[PPN][(Ph_3P)($C_2B_9H_{11}$)Ir{η^2-C(*p*-ClC_6H_4)NOC(=O)-} ([PPN·**2**]) 3,1,2-isomer	52	190	1650
[Et_4N][(Ph_3P)($C_2B_9H_{11}$)Rh{η^2-C(C_6H_5)NOC(=O)-} ([Et_4N]·**4a**) 3,1,2-isomer	50	103	1670
K[18-crown-6][(Ph_3P)($C_2B_9H_{11}$)Rh{η^2-C(*m*-FC_6H_4)NOC(=O)-} (K[18-crown-6]·**5a**) 3,1,2-isomer	76	213	1660
[Et_4N][(Ph_3P)($C_2B_9H_{11}$)Rh{η^2-C(*m*-PC_6H_4)NOC(=O)-} ([Et_4N]·**5b**) 2,1,7-isomer	60	118	1670
(η^5-C_5Me_5)(CO)Ir{η^2-C(2,4,6-$Me_3C_6H_2$)NOC(=O)-} (**6**)	65	105	1706
(η^5-C_5Me_5)(CO)Ir{η^2-C(*p*-ClC_6H_4)NOC(=O)-} (**7**)	87	142	1698
K[18-crown-6][$(CO)_4$Re{η^2-C(C_6H_5)NOC(=O)-} (K[18-crown-6]·**8**)	75	155	1640
(η^5-C_5Me_5)(PMe_3)Rh{η^2-C(*p*-FC_6H_4)NOC(=O)-} (**9**)	82	115	1689
(η^5-C_5Me_5)(CO)Rh{η^2-C(*p*-ClC_6H_4)NOC(=O)-} (**10**)	66	25	1690
(η^5-C_5H_5)(Ph_3P)Ir{η^2-C(*p*-ClC_6H_4)NOC(=O)-} (**12**)	80	167	1664
(η^5-C_5H_5)(Ph_3P)Ir{η^2-C(*p*-FC_6H_4)NOC(=O)-} (**13**)	75	162	1666
(η^5-C_5H_5)(Ph_3P)Rh{η^2-C(*p*-FC_6H_4)NOC(=O)-} (**14**)	60	115	1672
(η^5-C_5H_5)(Ph_3P)Co{η^2-C(*p*-ClC_6H_4)NOC(=O)-} (**15**)	60	20	1675

[a] Melting points were carried out in sealed tubes and are uncorrected. All metallacycles decompose at the melting point; decomposition temperatures are given when this preceded the melting point.

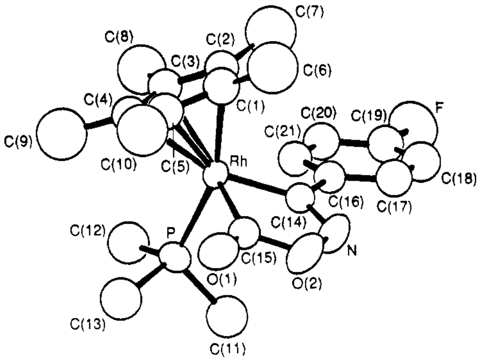

Figure 2. ORTEP projection of the metallacycle (η^5-C_5Me_5)(PMe_3)Rh{η^2-C(*p*-FC_6H_4)NOC(=O)-} (**9**). Hydrogen atoms have been omitted for clarity.

metallacycles as well, appeared to decompose relatively rapidly in halogenated solvents such as dichloromethane, and these solvents were avoided in the preparation of these metallacycles. Dichloromethane solutions of [Et_4N]·**4a** reacted with the solvent to produce a new red species, which, on the basis of its spectroscopic and analytical data, was formulated as the known [Et_4N][*closo*-3-(PPh_3)-3,3-$(Cl)_2$-3,1,2-Rh($C_2B_9H_{11}$)].[24] The mode of formation of this salt from metallacycle **4a**$^-$ is not evident at this time.

X-ray Crystal Structure of (η^5-C_5Me_5)(PMe_3)Rh{η^2-C(p-FC_6H_4)NOC(=O)-} (9). In order to obtain another example of the molecular structure of these metallacycles, crystals of the metallacycle (η^5-C_5Me_5)(PMe_3)Rh{η^2-C(*p*)FC_6H_4)NOC(=O)-} (**9**) were grown by vapor diffusion of pentane into an acetone solution of **9**. A suitable crystal was selected, and a single-crystal X-ray diffraction study was undertaken. An ORTEP projection of **9** is shown in Figure 2, and Table I lists the relevant bond distances and bond angles. The structure is that of the expected cycloadduct formed by reaction of *p*-fluorobenzonitrile *N*-oxide with (η^5-C_5Me_5)(PMe_3)Rh(CO). As in the molecular structure of PPN·**5b** (Figure 1), the rhodium center of complex **9** is pseudo-six-coordinate. The internal bond lengths and bond angles of the planar metallacycle are very similar to the values determined for PPN·**5b**. The Rh–C(14) bond length of 2.021 (5) and the Rh–C(15) bond length of 1.998 (5) are very short for rhodium–alkyl σ bonds.[21] The values obtained are nearly equal to those obtained for PPN·**5b**, indicating π-back-bonding from the Rh center to suitable orbitals of the chelate ligand.

Scope of the Cycloaddition Reaction. A number of metallacycles have been prepared by reaction of low-valent metal carbonyl complexes with aryl nitrile *N*-oxides (Table III). The reaction is not limited to metal carbonyl complexes containing η^5-dicarbollide or η^5-cyclopentadienyl complexes. As an example, when an orange solution of K[18-crown-6][$Re(CO)_5$] was treated with an ether solution of benzonitrile *N*-oxide, the white cycloadduct K[18-crown-6][$(CO)_4$Re{η^2-C(C_6H_4)NOC(=O)-}] (K[18-crown-6]·**8**) was produced. The manganese analogue K[18-crown-6][$Mn(CO)_5$] was also observed to react with benzonitrile *N*-oxide although the cycloadduct obtained proved to be too unstable to be satisfactorily characterized. Metallacycles involving first-row transition metals appeared to be very unstable, which is probably a manifestation of the weaker bonds formed between first-row transition metals and main-group elements when compared to the corresponding second- and third-row transition-metal bond strengths.

As shown above, a number of metallacycles have been synthesized by reactions of aryl nitrile *N*-oxides with a variety of low-valent metal carbonyl complexes. The synthesis of these metallacycles proceeded in good yields ranging between 50 and 85% and the precise conditions employed depended upon the nitrile *N*-oxide used and the thermal stability of the resulting metallacycle. In most cases the reaction temperature was maintained between 15 and 20 °C and a solution of the hydroxamic acid chloride was added slowly to a solution of the metal carbonyl complex in the presence of K_2CO_3. These conditions appeared to be optimal for conversion of the metal carbonyl complex to metallacycle and at the same time reduced the competitive dimerization of the nitrile oxide which complicated purification of the product. In general, the resulting metallacycles were polar and insoluble in nonpolar hydrocarbon solvents and could be readily recrystallized by using a suitable solvent combination. The ease and high yield with which these cycloaddition reactions occur is somewhat surprising in view of the ability of many nitrile *N*-oxides to function as oxidizing agents.[25]

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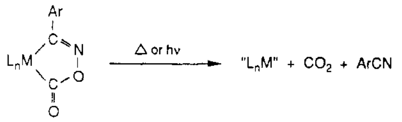
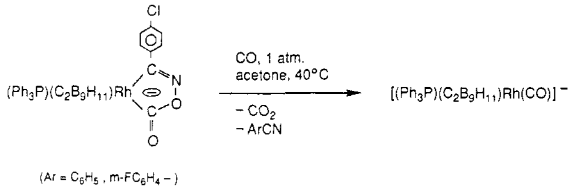
Scheme VI



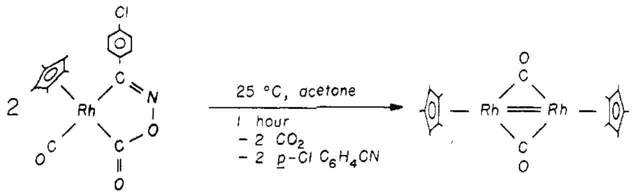
Scheme VII



Nitrile *N*-oxides are known to readily oxidize both free and coordinated phosphines to phosphine oxides while the nitrile oxide is reduced to the nitrile.[25a,b] Cobalt octacarbonyl also reduces nitrile oxides to nitriles, demonstrating the ability of nitrile *N*-oxides to serve as oxidizing agents with more complex metal carbonyl complexes.[25c] The success of these metallacycle syntheses, employing reactions between a reducing low-valent metal carbonyl complex and an aryl nitrile *N*-oxide, must be a result of the reactivity of the unsaturated M–CO bond and the resulting stabilization afforded the metallacycle products.

Chemical Reactivity and Thermal Stability of Metallacycles. As mentioned earlier, certain metallacycles appeared to be thermally unstable in solution, even at room temperature. On an a priori basis, thermolysis of a metallacycle would be expected to readily occur and result in the loss of carbon dioxide and free nitrile ligand to generate a highly reactive metal fragment, "ML_n", which would be both electronically and coordinatively unsaturated (Scheme VI). Thus, mild thermolysis or photolysis of these metallacycles suggested a potentially versatile method of producing highly reactive metal complex fragments in solution without encountering a high activation energy, since formation of the very stable carbon dioxide and the aryl nitrile molecules provided a strong thermodynamic driving force for decomposition of the metallacycles. Initial studies of the mode of decomposition of the metallacycles and the nature of the products obtained suggested that thermolysis of solutions of these metallacycles did indeed result in the release of reactive metal complex fragments as outlined in Scheme VI. When acetone solutions of the metallacycles **5a**$^-$ and **5b**$^-$ were maintained at 40 °C under an atmosphere of carbon monoxide, the starting rhodacarborane carbonyl anions **3a**$^-$ and **3b**$^-$, respectively, were quantitatively regenerated (Scheme VII). In a formal sense this may occur by reaction of carbon monoxide with the presumed 16-electron, four-coordinate metal fragment "$(PPh_3)Rh(C_2B_9H_{11})^-$" generated in situ by loss of carbon dioxide and *m*-fluorobenzonitrile from **5a**$^-$ and **5b**$^-$. The rhodium metallacycle $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh\{\eta^2\text{-}C(p\text{-}ClC_6H_4)NOC(=O)\text{-}\}$ (**10**) is also thermally labile in solution, as shown by the fact that a yellow THF solution of **10** becomes dark blue upon standing at 25 °C and affords the known dimeric complex $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CO)]_2$ (**11**)[26] (Scheme VIII). The rhodium dimer was obtained by the presumed dimerization of the metal fragment "$(\eta^5\text{-}C_5Me_5)Rh(CO)$". The dinuclear complex **11** has also been prepared in high yield by reaction of $(\eta^5\text{-}C_5Me_5)Rh(CO)_2$ and trimethylamine *N*-oxide.[9c,e] Trimethylamine *N*-oxide has frequently been used to remove terminal carbonyl ligands through nucleophilic attack at the carbonyl carbon and subsequent loss of carbon dioxide to produce unsaturated reactive metal fragments.[27] Our initial results demonstrate that formation and subsequent thermolysis of the metallacycles described here provides another method of removing coordinated terminal carbonyl ligands to generate reactive metal fragments in solution. Since we have already communicated our initial results obtained from the thermolysis of metallacycles **12**, **13**[8a] and **7**, **9**[8b] and a full report will follow shortly,[8c] further details concerning the reactivity and nature of the products formed on thermolysis of these metallacycles will not be given here.

Scheme VIII



The metallacycles synthesized in this study (Table III) demonstrate a wide range of thermal stabilities. The metallacycle $(\eta^5\text{-}C_5H_5)(PPh_3)Ir\{\eta^2\text{-}C(p\text{-}ClC_6H_4)NOC(=O)\text{-}\}$ (**12**) decomposes over a period of 24 h at 110 °C in toluene, whereas orange solutions of the cobalt analogue $(\eta^5\text{-}C_5H_5)(PPh_3)Co\{\eta^2\text{-}C(p\text{-}ClC_6H_4)NOC(=O)\text{-}\}$ (**15**) darken to a red-brown coloration almost instantaneously when maintained above 20 °C. The cobalt metallacycle **15** is also very unstable in the solid state, and analytical data could not be obtained for this compound. The rhodium congener $(\eta^5\text{-}C_5H_5)(PPh_3)Rh\{\eta^2\text{-}C(p\text{-}FC_6H_4)NOC(=O)\text{-}\}$ (**14**) in this series has intermediate thermal stability when compared to the cobalt and iridium analogues since solutions of **14** decompose slowly at room temperature over 24 h. The range of thermal stabilities observed in metallacycles **12**–**14** probably reflects the relative bond strengths of first–, second–, and third-row transition metals with main-group elements. Another factor that undoubtedly has an important influence on the stability of these metallacycles is the degree of π-back-bonding from the metal center to acceptor orbitals within the chelated ligand. As already pointed out in the discussion of the molecular structures of PPN·**5b** and **9**, the planarity of the five-membered metallacycle and the very short rhodium–carbon bond lengths between the rhodium center and the two carbons of the chelate ligand suggest substantial π-back-bonding from the metal. The trend that the more electron-rich and/or sterically encumbered the metal center the more stable the resulting metallacycle is exemplified by the relative stabilities of metallacycles **9** and **10** which are obtained from the respective rhodium carbonyl complexes $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(CO)$ and $(\eta^5\text{-}C_5Me_5)Rh(CO)_2$. The bulky trimethylphosphine ligand renders the rhodium center of complex **9** more electron-rich and the complex more thermally stable than the less electron-rich **10**. As mentioned above, when a THF solution of **10** was maintained at 25 °C, the pale yellow solution turned dark blue within 1 h and was converted to $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CO)]_2$ (**11**) (Scheme VI). Solutions of **9** showed more thermal stability in that a THF solution of **9** decomposed slowly over several hours when maintained at 30 °C. By varying the electronic and steric properties of the ancillary ligands about the metal and the metal center itself (whether first, second, or third row), the stability of the metallacycle can be greatly influenced, which, in turn, allows the reactions

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(27) Blumer, D. J.; Barnett, K. W.; Brown, T. L. *J. Organomet. Chem.* **1979**, *173*, 71.

of these cycloadducts to be studied under a wide variety of conditions.

Conclusions. As shown in this paper, the conversion of low-valent metal carbonyl complexes to metallacycles by 1,3-dipolar cycloaddition of aryl nitrile *N*-oxides to the M–CO bond occurs with ease and in high yield. We are planning to extend these reactions to other 1,3-dipolar reagents and also to other low-valent transition-metal complexes containing a multiple metal to ligand bond such as isonitrile complexes, metal oxides and sulfides, and metal carbene and carbyne complexes. We are also investigating the reactivity of the metallacycles described here during their thermolysis and photolysis in the presence of reactive substrates, a subject treated in the following paper.

Experimental Section

General Procedure. All reactions were routinely carried out under an atmosphere of dry and deoxygenated nitrogen by using Schlenk techniques. All solvents were distilled under nitrogen before use; tetrahydrofuran (THF) and diethyl ether were distilled from purple solutions of sodium benzophenone ketyl. Benzene, toluene, and heptane were distilled from potassium metal; pentane was first stirred for 48 h over concentrated H_2SO_4 and then distilled over calcium hydride, before finally distilling from a purple solution of sodium benzophenone ketyl. Methylene chloride and acetonitrile were distilled from P_2O_5, and methanol was distilled from magnesium methoxide. The metal carbonyl complexes $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$,[28] $(\eta^5\text{-}C_5Me_5)Rh(CO)_2$,[29] $(\eta^5\text{-}C_5Me_5)Rh(CO)(PMe_3)$,[29] $(\eta^5\text{-}C_5H_5)Ir(CO)(PPh_3)$,[30] $(\eta^5\text{-}C_5H_5)Rh(CO)(PPh_3)$,[30] and $(\eta^5\text{-}C_5H_5)Co(CO)(PPh_3)$[30] were all prepared according to literature procedures, as were the rhodacarborane anions[19b,c] $[\textit{closo}\text{-}3\text{-}(PPh_3)\text{-}3\text{-}(CO)\text{-}3,1,2\text{-}RhC_2B_9H_{11}]^-$ (**3a**$^-$) and $[\textit{closo}\text{-}2\text{-}(PPh_3)\text{-}2\text{-}(CO)\text{-}2,1,7\text{-}RhC_2B_9H_{11}]^-$ (**3b**$^-$) and the iridacarborane anion[19b] $[\textit{closo}\text{-}3\text{-}(PPh_3)\text{-}3\text{-}(CO)\text{-}3,1,2\text{-}IrC_2B_9H_{11}]^-$ (**1**$^-$). Pentamethylcyclopentadiene was prepared by literature procedures.[31] PPN^+Cl^- and 18-crown-6 were purchased from Aldrich Chemical Co. and used as received. Benzaldehyde, *m*- and *p*-fluorobenzaldehyde, *p*-chlorobenzaldehyde, and 2,4,6-trimethylbenzaldehyde were all commercially available and used as received to prepare the respective oximes.[32] Trimethylphosphine, triphenylphosphine, and $Re_2(CO)_{10}$ were all purchased from Strem Chemical Co. and used as received. Elemental analyses for compounds **4**, **5**, **8**, and **10** were all performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY; analyses for all other compounds were carried out by Galbraith Laboratories, Knoxville, TN. IR spectra for compounds [Et_4N·**4a**], K[18-crown-6]·**5**, K[18-crown-6]·**8**, and **10** were recorded on a Perkin-Elmer 137 instrument; the IR spectra of all other compounds were recorded on a Beckman FT-1100 instrument. ^1H NMR and $^{31}P\{^1H\}$ NMR spectra for compounds **4**, **5**, **8** and **10** were recorded on a Bruker WP-200 spectrometer; the ^{11}B NMR spectra of these compounds were recorded at 80.5, 111.80, and 121.01 MHz by using an instrument designed and constructed by Professor F. A. L. Anet and his co-workers. ^1H NMR and $^{31}P\{^1H\}$ NMR spectra for compounds **6**–**14** were recorded by using a JEOL FX-90 instrument. ^1H NMR chemical shifts were referenced relative to residual ^1H resonances in deuteriated solvents, ^{31}P chemical shifts were referenced to external 85% H_3PO_4, and ^{11}B chemical shifts were referenced to external $BF_3\cdot OEt_2$ where positive shifts refer to lower field.

Table IV. Details of Crystallographic Data Collection

	9	PPN·**5b**
temp/°C	25	25
cryst size/mm	0.4 × 0.4 × 0.5	0.08 × 0.2 × 0.3
normal to faces	100, 010, 001	110, 001, $\bar{2}10$
appearance	parallelepiped	platelet
radiatn (graphite monochromator)	Mo Kα	Mo Kα
wavelength/Å	0.7107	0.7107
space group	$P2_1/c$	$P\bar{1}$
a/Å	9.0376 (7)	12.910 (5)
b/Å	14.8675 (13)	13.270 (5)
c/Å	16.1965 (14)	18.402 (7)
α/deg	90	88.24 (3)
β/deg	99.074 (3)	109.46 (3)
γ/deg	90	83.89 (3)
V/Å^3	2149	2948
Z	4	2
ρ(calcd)/g cm^{-3}	1.48	1.37
μ/cm^{-1}	8.775	4.13
range of transmission factors	0.8552–0.8244 0.8444 (av)	0.9727–0.9478 0.9631 (av)
scan width		
below Kα_1	1.3	1.25
above Kα_2	1.6	1.25
scan rate/deg min^{-1}	6	8
no. of unique reflctns	3785	7743
no. of obsd ($I > 3\sigma(I)$) reflctns	3110	5701
2θ max/deg	50	45
data collected	$+h,+k,\pm l$	$+h,\pm k,\pm l$
no. of parameters refined	247	344
R,R_w,GOF	0.039,0.056,2.00	0.060,0.062,1.53

Crystallographic Measurements. Collection and Reduction of X-ray Data for $[PPN][\textit{closo}\text{-}2\text{-}(PPh_3)\text{-}2\text{-}\{\eta^2\text{-}C(\textit{m}\text{-}FC_6H_4)NOC(=O)\text{-}\}\text{-}2,1,7\text{-}RhC_2B_9H_{11}]$ (PPN·5b). An air-stable crystal was mounted on a thin glass fiber on a Syntex P$\bar{1}$ diffractometer. Unit cell parameters were determined from a least-squares fit of 15 accurately centered reflections ($11 < 2\theta < 22$). These dimensions and other parameters, including conditions of data collection, are summarized in Table IV. Data were collected in the θ–2θ scan mode. Three intense reflections ($1\bar{4}\bar{1}$, 302, 441) were monitored every 97 reflections to check stability. The intensity of these reflections fluctuated only slightly, ca. ±4%, during the course of the experiment. Of the 7743 unique reflections measured, 5701 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz, polarization, and absorption effects.

Solution and Refinement of the Structure of $[PPN][\textit{closo}\text{-}2\text{-}(PPh_3)\text{-}2\text{-}\{\eta^2\text{-}C(\textit{m}\text{-}FC_6H_4)NOC(=O)\text{-}\}\text{-}2,1,7\text{-}RhC_2B_9H_{11}]$ (PPN·5b). Atoms were located by use of the heavy-atom method. All calculations were performed on the VAX 11/780 computer of this department. All phenyl groups of the phosphines were treated as rigid C_6H_5 hexagons, C–C = 1.395 Å and C–H = 1.0 Å. All remaining hydrogen atoms were located and included in the least-squares refinement. Anisotropic thermal parameters were included for all anionic non-hydrogen atoms, with exception of the carborane ligand and the phenyl groups of the phosphine ligand. Isotropic thermal parameters were refined for all other non-hydrogen atoms and for the four hydrogen atoms of the fluorophenyl group. A single thermal parameter was refined for hydrogen atoms of the carborane ligand. Three thermal parameters were refined for hydrogen of the phenyl groups, for hydrogen ortho, meta, or para to the carbon atom attached to phosphorus. Scattering factors and anomalous dispersion terms were taken from ref 33 and 34. A final difference electron density map was relatively featureless; the maximum peaks are about 0.7–0.8 e Å^{-3} and are located near para carbon atoms. Final positional and thermal parameters for non-hydrogen atoms are given in Table II. Programs used in this work included locally modified versions of the following programs: CARESS (Broach, Coppens, Becker and Blessing), peak profile analysis, Lorentz and polarization corrections; ORTEP (Johnson), figure plotting; and SHELX76 (Sheldrick), structure analysis package.

Collection and Reduction of X-ray Data for $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh\{\eta^2\text{-}C(\textit{p}\text{-}FC_6H_4)NOC(=O)\text{-}\}$ (9). An air-stable crystal,

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obtained from an acetone/pentane solution, was mounted on a thin glass fiber on a diffractometer constructed by Professor C. E. Strouse of this department. Systematic absences were found for reflections $0k0, k = 2n + 1$, and $h0l, l = 2n + 1$. Unit cell parameters were determined from a least-squares fit of 38 accurately centered reflections ($10 < 2\theta < 20°$). These dimensions and other parameters, including conditions of data collection, are summarized in Table IV. Data were collected in the θ–2θ scan mode. Three intense reflections ($\bar{1}25$, 223, $\bar{3}30$) were monitored every 97 reflections to check stability. Intensities of these reflections fluctuated only slightly, ca. ±3%, during the course of the experiment. Of the 3785 unique reflections measured, 3110 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz, polarization, and absorption effects.

Solution and Refinement of the Structure of (η^5-C_5Me_5)(PMe_3)Rh{η^2-C(*p*-FC_6H_4)NOC(=O)-} (9). Atoms were located by use of the heavy-atom method. All calculations were performed on the Vax 11/750 crystallographic computer. All phenyl and methyl hydrogen atoms were included in calculated positions, C–H = 1.0 Å and methyl H–C–H = 109.5°, with assigned U values of 0.08 Å^2 for phenyl H. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Scattering factors for H were obtained from Stewart et al.[33] and for other atoms were taken from ref 34. Anomalous dispersion terms were applied to the scattering of Rh and P. A final difference electron density map was essentially featureless, the maximum peak being about 0.6 e/Å^3. Final positional and thermal parameters for non-hydrogen atoms are given in Table II.

Preparation of Hydroxamic Acid Chlorides. Benzohydroxamic acid chlorides, *m*- and *p*-fluorobenzohydroxamic acid chloride, and *p*-chlorobenzohydroxamic acid chloride were all prepared by chlorination of the corresponding oxime with the following general procedure. About 5 g of the oxime was dissolved in 300 mL of chloroform at −20 to −15 °C. Chlorine gas was then slowly bubbled through the solution producing a transient blue coloration; the slow addition of chlorine was continued for about 20 min, while the temperature was maintained between −20 to −15 °C. The solution was purged with a stream of N_2 removing excess chlorine until it had warmed to room temperature. The solvent was then removed under a reduced pressure to yield the crude hydroxamic acid chloride which was frequently used without recrystallization. A list of melting points for several of these hydroxamic acid chlorides can be found in the literature.[35] The stable nitrile oxide, 2,4,6-trimethylbenzonitrile oxide was prepared by a published procedure.[23]

Preparation of [PPN][*closo*-3-(PPh_3)-3-{η^2-C(*p*-ClC_6H_4)-NOC(=O)-}-3,1,2-$IrC_2B_9H_{11}$] ([PPN]·2]). A solution of 0.30 g (1.8 mmol) of *p*-$ClC_6H_4C(Cl)NOH$ in 20 mL THF was added dropwise over a period of 2 h to a suspension of 1.9 g (0.16 mmol) of [PPN][*closo*-3-(PPh_3)-3-(CO)-3,1,2-Ir($C_2B_9H_{11}$)](PPN·1) and 0.3 g of anhydrous Na_2CO_3 in 30 mL of THF at room temperature. The color of the suspension becomes lighter as the reaction proceeds. The solution was filtered, and a pale yellow solution was obtained yielding a pale yellow solid on addition of pentane. The product was recrystallized from THF–ether to yield analytically pure product: yield 1.09 g (52%); mp 190 °C dec. Anal. Calcd for $C_{64}H_{60}B_9ClIrN_2O_2P_3$: C, 58.80; H, 4.64; B, 7.44; Ir, 14.70; N, 2.14; P, 7.10. Found: C, 58.71; H, 4.75; B, 7.14; Ir, 14.42; N, 2.00; P, 6.84. IR (Nujol): 2543 (vs), 1650 (vs), 1590 (m), 1285 (vs, br), 1186 (m), 1165 (w), 1115 (vs), 1100 (s), 998 (s), 861 (m), 831 (w), 746 (s), 724 (vs), 693 (vs) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 8.61–7.21 (complex multiplets, 49 H), 2.74 (s, 1 H, carboranyl C–H), 1.83 (s, 1H, carboranyl C–H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 22.67, 5.32.

Preparation of [Et_4N][*closo*-3-(PPh_3)-3-{η^2-C(C_6H_5)NOC-(=O)-}-3,1,2-$RhC_2B_9H_{11}$] (Et_4N·4a). To a precooled (−78 °C) suspension of a 0.400 g (0.61 mmol) of [Et_4N]·3b and 0.3 g of anhydrous K_2CO_3 in 100 mL of CH_2Cl_2 was added 0.11 g (0.71 mmol) of benzohydroxamic acid chloride. The mixture was allowed to warm to 15 °C over a period of 2 h producing an orange-colored solution. After this solution was filtered, 50 mL of MeOH was added and the solution was concentrated in vacuo to 25 mL. The pale orange solid obtained was then rinsed with MeOH and ether. Recrystallization of this solid from CH_2Cl_2–MeOH and acetonitrile–ether at −20 °C produced analytically pure material: yield 0.23 g (50%); mp 103 °C dec. Anal. Calcd for $C_{36}H_{57}B_9N_2O_2PRh$: C, 55.80; H, 6.63; B, 12.56; N, 3.62; P, 4.00; Rh, 13.28. Found: C, 56.02; H, 6.92; B, 12.22; N, 3.48; P, 4.06; Rh, 13.18. IR (Nujol): 2500 (vs), 1670 (vs), 1520 (m), 1235 (w), 1180 (m), 1095 (s), 1075 (w), 1065 (w), 1040 (s), 1035 (ms), 1000 (s, br), 980 (s), 955 (w), 930 (w), 895 (w), 865 (m, br), 795 (w), 755 (s), 765 (s), 720 (m), 705 (vs, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2, −73 °C): δ 7.3–6.98 (complex multiplets, 20 H), 3.32 (q, 8 H, CH_2 of cation), 1.42 (s, 1 H, carboranyl C–H), 1.26 (s, 1 H, carboranyl C–H), 1.20 (t, 12 H, CH_3 of cation). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −73 °C): δ 26.5 (d, J_{Rh-P} = 120 Hz).

Preparation of K[18-crown-6][*closo*-3-(PPh_3)-3-{η^2-C(*m*-FC_6H_4)NOC(=O)-}-3,1,2-$RhC_2B_9H_{11}$] (K[18-crown-6]·5a). To a suspension of 0.700 g (0.84 mmol) of K[18-crown-6]·3a and 0.5 g of anhydrous K_2CO_3 in 70 mL of CH_2Cl_2 cooled to −78 °C was added 0.40 g (2.2 mmol) of *m*-$FC_6H_4C(Cl)NOH$. The reaction was allowed to warm to 15 °C over a period of 3 h producing a lemon-yellow solution. After the solution was filtered, the product was precipitated, by the addition of excess diethyl ether, as lemon-yellow crystals. An analytically pure sample was obtained by recrystallization of the reaction product twice from acetone-ether at −20 °C: yield 0.61 g (76%); mp 213 °C. Anal. Calcd for $C_{40}H_{54}B_9FKNO_8PRh$: C, 49.73; H, 5.63; B, 10.07; F, 1.97; K, 4.05; N, 1.45; P, 3.20; Rh, 10.65. Found: C, 49.74; H, 5.93; B, 10.16; F, 1.98; K, 4.15; N, 1.63; P, 3.39; Rh, 10.63. IR (Nujol): 2500 (vs), 1660 (vs), 1610 (m), 1595 (m), 1520 (m), 1280 (s), 1265 (s), 1245 (m), 1190 (w), 1100 (vs, br), 980 (vs, br), 960 (vs), 880 (w), 845 (vs), 795 (s), 760 (s), 750 (s), 700 (vs, br) cm^{-1}. ^{1}H NMR (CD_3COCD_3, −73 °C): δ 7.77–6.78 (complex multiplets, 19 H), 3.51 (s, 24 H, CH_2 of cation), 2.72 (s, 1 H, carboranyl C–H). $^{31}P\{^1H\}$ NMR (CD_3COCD_3, −73 °C): δ 37.5 (d, J_{Rh-P} = 134 Hz).

Preparation of [Et_4N][*closo*-2-(PPh_3)-2-{η^2-C(*m*-FC_6H_4)-NOC(=O)-}-2,1,7-$RhC_2B_9H_{11}$] ([Et_4N]·5b). A suspension of 0.500 g (0.76 mmol) of [Et_4N]·3b and 0.3 g of anhydrous K_2CO_3 in 70 7L of CH_2Cl_2 was cooled to −78 °C. To this suspension was added 0.19 g (1.1 mmol) of *m*-$FC_6H_4C(Cl)NOH$. The reaction was allowed to warm to 0 °C over a period of 2 h. The solution was filtered and diluted with an excess of 50% ether–pentane producing a white solid. The solid was recrystallized from CH_3CN–ether and CH_2Cl_2–ether at −20 °C producing analytically pure material: yield 0.36 g (60%); mp 118 °C. Anal. Calcd for $C_{36}H_{50}B_9FNO_2PRh$: C, 54.53; H, 6.35; B, 12.27; F, 2.39; N, 3.53; P, 3.90; Rh, 12.98. Found: C, 54.79; H, 6.55; B, 11.80; F, 2.68; N, 3.68; P, 3.60; Rh, 12.50. IR (Nujol, PPN$^+$·4): 2500 (s), 1670 (s), 1575 (w), 1560 (m), 1520 (w), 1175 (ms), 1160 (w), 1145 (w), 1100 (vs, br), 1090 (s), 1075 (m), 1025 (w), 995 (vs), 885 (m), 835 (vs), 806 (m), 785 (m), 755 (vs, br), 745 (vs, br), 725 (vs, br), 695 (vs, br) cm^{-1}. ^{1}H NMR (CD_3COCD_3, −73 °C): δ 7.78–6.97 (complex multiplets, 49 H), 1.59 (s, 1 H, carboranyl C–H), 1.26 (s, 1 H, carboranyl C–H). $^{31}P\{^1H\}$ NMR (CD_3COCD_3, −73 °C): δ 29.5 (d, J_{Rh-P} = 122 Hz).

Preparation of (η^5-C_5Me_5)(CO)Ir{η^2-C(2,4,6-$Me_3C_6H_2$)-NOC(=O)-} (6). To a solution of 0.20 g (0.52 mmol) of (η^5-C_5Me_5)Ir$(CO)_2$ in 30 mL of THF was added 0.10 g (0.58 mmol) of 2,4,6-$Me_3C_6H_2CNO$; the yellow solution was stirred at room temperature for eight hours, becoming colorless as the reactants were consumed. After filtering and concentrating in vacuo pentane was added producing a white solid: yield 0.12 g, 65%; mp 105 °C. Analytically pure product could be obtained by recrystallization from THF–ether. Anal. Calcd for $C_{22}H_{26}IrO_3N$: C, 48.51; H, 4.82; Ir, 35.29; N, 2.57. Found: C, 48.67; H, 4.90; Ir, 35.58; N, 2.55. IR (Nujol): 2014 (vs), 1819 (w), 1706 (vs), 1608 (m), 1561 (m), 1384 (w), 1260 (w), 1160 (w), 1075 (m), 1032 (s), 989 (vs), 920 (m), 842 (vs), 680 (w), 642 (w), 620 (s) cm^{-1}. ^{1}H NMR (C_6D_6): δ 6.78 (s, 1 H), 6.71 (s, 1 H), 2.30 (s, 3 H), 2.22 (s, 3 H), 2.16 (s, 3 H), 1.25 (s, 15 H).

Preparation of (η^5-C_5Me_5)(CO)Ir{η^2-C(*p*-ClC_6H_4)NOC-(=O)-} (7). A suspension of 0.58 g (1.5 mmol) of (η^5-C_5Me_5)Ir-$(CO)_2$ and 0.3 g of anhydrous Na_2CO_3 in 20 mL of THF was maintained at 20 °C; to this suspension was added a solution of 0.32 g (1.7 mmol) of *p*-$ClC_6H_4C(Cl)NOH$ in 20 mL of THF slowly over a period of 5 h. The color changed from yellow to white as the reaction proceeded. The colorless solution was filtered, and the Na_2CO_3 was washed several times with CH_2Cl_2

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to recover that portion of the product which adsorbs onto the Na_2CO_3. The washings were combined with the THF solution and the solvents removed in vacuo. The white residue was dissolved in CH_2Cl_2 and filtered; addition of pentane yielded a white solid: yield 0.67 g (87%); mp 142 °C dec. Analytically pure product could be obtained by recrystallization from CH_2Cl_2–pentane at −20 °C. Anal. Calcd for $C_{19}H_{19}ClIrNO_3$: C, 42.57; H, 3.58; Ir, 35.85; N, 2.61. Found: C, 42.12; H, 3.64; Ir, 35.88; N, 2.40. IR (Nujol): 2020 (vs), 1698 (vs), 1652 (w), 1590 (w), 1568 (m), 1532 (m), 1498 (m), 1483 (s), 1276 (w), 1246 (w), 1176 (w), 1108 (w), 1088 (s), 1032 (w), 1010 (m), 987 (vs), 961 (m), 850 (vs), 835 (s), 744 (w), 718 (w), 666 (w), 638 (m), 620 (m) cm^{-1}. ^1H NMR (C_6D_6): δ 7.39–7.38 (m, 2 H), 7.10–7.08 (s, 2 H), 1.26 (s, 15 H).

Preparation of K[18-crown-6][$(CO)_4Re\{\eta^2\text{-}C(C_6H_5)NOC(=O)-\}$ (K[18-crown-6]·8). A solution of 0.500 g (0.76 mmol) of $Re_2(CO)_{10}$ in 100 mL of THF was reduced with excess dilute (0.5%) K(Hg) in the presence of 0.40 g (1.52 mmol) of 18-crown-6 producing an orange-yellow solution in 3 h. The solution was filtered away from the amalgam and then refiltered to produce a clear orange-yellow solution. The solution was cooled to −78 °C and to it was added an ether solution of benzonitrile *N*-oxide at −50 °C formed from 0.35 g (2.26 mmol) of benzohydroxamic acid chloride and 0.6 g of anhydrous K_2CO_3. Warming the reaction to 0 °C produced a very pale solution which was refiltered. To the solution was added 500 mL of 50% ether–pentane to precipitate a white microcrystalline product: yield 0.85 g (75%); mp 155 °C dec. An analytically pure sample was obtained by recrystallizing the reaction product several times from CH_2Cl_2–ether–pentane. Anal. Calcd for $C_{24}H_{29}KNReO_{12}$: C, 38.50; H, 3.90; K, 5.22; N, 1.87; Re, 24.87. Found: C, 38.63; H, 3.88; K, 5.36; N, 1.92; Re, 24.39. IR (Nujol): 2060 (m), 2040 (m), 1930 (vs), 1640 (vs), 1275 (m), 1250 (m), 1100 (vs), 965 (vs), 845 (vs), 825 (vs), 770 (m), 705 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.31–7.1 (m, 5 H), 3.51 (s, 24 H, CH_2 of cation).

Preparation of $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh\{\eta^2\text{-}C(p\text{-}FC_6H_4)NOC(=O)-\}$ (9). A suspension of 0.40 g (1.2 mmol) of $(\eta^5\text{-}C_5Me_5)$-$Rh(CO)(PMe_3)$ and 0.3 g of anhydrous Na_2CO_3 in 30 mL of THF was maintained at 20 °C. To this suspension a solution of 0.28 g (1.6 mmol) of *p*-$FC_6H_4C(Cl)NOH$ in 20 mL of THF was added over a period of 10 h. The suspension turned orange when the reaction was complete; the solution was filtered and the THF removed in vacuo. The orange solid was washed with ether and pentane and then redissolved in 30 mL of acetone. The solution was filtered, and on addition of 100 mL of pentane, an orange solid was obtained: yield 0.46 g (82%); mp 115 °C dec. An analytically pure sample of 8 was obtained by slow recrystallization of an acetone solution with pentane at −20 °C. Anal. Calcd for $C_{31}H_{24}FNOPRh$: C, 52.61; H, 5.89; N, 2.92; P, 6.46; Rh, 21.47. Found: C, 52.40; H, 6.02; N, 2.77; P, 6.32; Rh, 21.02. IR (Nujol): 1689 (vs), 1599 (m), 1498 (m), 1310 (w), 1283 (w), 1231 (m), 1213 (m), 1152 (m), 984 (s), 946 (s), 856 (m), 832 (m), 837 (m), 815 (w), 735 (w), 720 (w), 680 (w) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 7.61–7.00 (complex multiplets, 19 H), 1.63 (d, J = 2.4 Hz, 15 H), 1.37 (dd, J = 10.5, 1.0 Hz, 9 H). $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ 1.98 (d, J = 144.0 Hz).

Preparation of $(\eta^5\text{-}C_5Me_5)(CO)Rh\{\eta^2\text{-}C(p\text{-}ClC_6H_4)NOC(=O)-\}$ (10). A solution of 0.250 g (0.84 mmol) of $(\eta^5\text{-}C_5Me_5)$-$Rh(CO)_2$ in 30 mL of CH_2Cl_2 was cooled to −78 °C; to this was added 0.40 g of anhydrous K_2CO_3 and 0.23 g (1.2 mmol) of *p*-$ClC_6H_4C(Cl)NOH$. The reaction was then allowed to warm to −10 °C producing a pale yellow solution. The solution was then concentrated in vacuo at 0 °C. The resultant pale yellow precipitate was isolated, rinsed with cold pentane, and dried in vacuo; yield 0.25 g (66%). Due to the instability of this compound, elemental analyses could not be obtained. IR (Nujol): 2020 (vs), 1690 (vs), 1575 (w), 1550 (m), 1530 (w), 1240 (m), 1175 (w), 1110 (w), 1080 (s), 1060 (w), 1035 (w), 1020 (m), 980 (vs, br), 855 (vs), 835 (vs), 750 (m), 730 (w) cm^{-1}.

Preparation of $(\eta^5\text{-}C_5H_5)(PPh_3)Ir\{\eta^2\text{-}C(p\text{-}ClC_6H_4)NOC(=O)-\}$ (12). A suspension of 1.0 g (1.44 mmol) of $(\eta^5\text{-}C_5H_5)Ir(CO)(PPh_3)$ and 0.3 of anhydrous Na_2CO_3 in 30 mL of THF was maintained at 20 °C. A solution of 0.30 g (1.58 mmol) of *p*-$ClC_6H_4C(Cl)NOH$ in 20 mL of THF was added to the suspension over a period of 6 h. The color of the suspension became pale yellow; the solution was filtered, and after concentration in vacuo, a pale yellow solid was precipitated by addition of 50 mL of pentane: yield 1.01 g (80%); mp 167 °C dec. Analytically pure samples could be obtained by recrystallization from CH_2Cl_2–pentane and THF–ether. Anal. Calcd 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. IR (Nujol): 1664 (vs), 1587 (w), 1567 (w), 1498 (m), 1483 (s), 1311 (w), 1235 (w), 1184 (w), 1170 (w), 1096 (s), 1022 (m), 1000 (vs), 875 (s), 851 (m), 835 (m), 820 (m), 749 (m), 710 (s), 695 (vs), 675 (w), 639 (s), 616 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.37–7.15 (complex multiplets, 19 H), 5.39 (d, J = 1.0 Hz, 5 H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −2.22.

Preparation of $(\eta^5\text{-}C_5H_5)(PPh_3)Ir\{\eta^2\text{-}C(p\text{-}FC_6H_4)NOC(=O)-\}$ (13). To a solution of 0.60 g (1.1 mmol) of $(\eta^5\text{-}C_5H_5)Ir(CO)(PPh_3)$ in 25 mL of THF was added 0.3 g of anhydrous Na_2CO_3. The suspension was maintained at 20 °C, and a solution of 0.23 g (1.3 mmol) of *p*-$FC_6H_4C(Cl)NOH$ in 15 mL of THF was added over a period of 5 h. The solution became lighter eventually turning colorless; it was filtered and the THF removed in vacuo. The product was dissolved in 25 mL of CH_2Cl_2 and filtered; addition of 50 mL of pentane gave a white solid. Recrystallization from CH_2Cl_2–pentane gave analytically pure white crystals of **13**: yield 0.56 g (75%); mp 162 °C dec. Anal. Calcd for $C_{31}H_{24}FIrNO_2P$: 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. IR (Nujol): 1666 (vs), 1596 (m), 1500 (s), 1230 (m), 1216 (m), 1182 (m), 1095 (s), 1068 (w), 1028 (w), 1000 (s), 878 (s), 840 (s), 810 (m), 749 (m), 707 (s), 695 (s), 640 (m), 617 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.46–6.74 (complex multiplets, 19 H), 5.39 (d, J = 1.0 Hz, 5 H). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$): δ −2.09.

Preparation of $(\eta^5\text{-}C_5H_5)(PPh_3)Rh\{\eta^2\text{-}C(p\text{-}FC_6H_4)NOC(=O)-\}$ (14). A suspension of 0.40 g (0.87 mmol) of $(\eta^5\text{-}C_5H_5)$-$Rh(CO)(PPh_3)$ in 30 mL of THF and 0.3 g of anhydrous Na_2CO_3 was maintained at 20 °C. To this suspension was added a solution of 0.17 g (0.96 mmol) of *p*-$FC_6H_4C(Cl)NOH$ in 20 mL of THF over a period of 5 h. The color changed from orange to yellow, the solution was filtered, and addition of 100 mL of pentane yielded a yellow solid: yield 0.31 g (60%); mp 115 °C. An analytically pure sample could be obtained by recrystallization from CH_2Cl_2–pentane to yield yellow crystals of 14. Anal. Calcd for $C_{31}H_{24}FNO_2PRh$: C, 62.53; H, 4.07; N, 2.35; P, 5.20; Rh, 17.28. Found: C, 62.25; H, 3.94; N, 2.25; P, 5.04; Rh, 16.97. IR (Nujol): 1672 (s), 1593 (w), 1515 (w), 1497 (m), 1227 (m), 1155 (m), 966 (m), 865 (m), 835 (m), 808 (m), 748 (m), 708 (m), 694 (s) cm^{-1}. ^1H NMR (C_6D_6): δ 7.73–6.50 (complex multiplets, 19 H), 4.97 (dd, J = 1.2, 0.5 Hz, 5 H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 38.63 (d, J = 161.1 Hz).

Preparation of $(\eta^5\text{-}C_5H_5)(PPh_3)Co\{\eta^2\text{-}C(p\text{-}ClC_6H_4)NOC(=O)-\}$ (15). A suspension of 0.40 g (0.96 mmol) of $(\eta^5\text{-}C_5H_5)$-$Co(CO)(PPh_3)$ and 0.3 g of anhydrous Na_2CO_3 in 30 mL of THF was maintained at 15 °C. To this suspension was added a solution of 0.18 g (0.96 mmol) of *p*-$ClC_6H_4C(Cl)NOH$ in 20 mL of THF over a period of 6 h. The color turned to orange as the reaction proceeded. The solution was filtered and concentrated in vacuo; addition of pentane at 0 °C yielded a yellow-orange product which could be recrystallized from CH_2Cl_2–ether. The product decomposes instantaneously in solution above 20 °C. Since the solid was also very thermally unstable, analytical data could not be obtained for it. Yield: 0.33 g (60%). IR (Nujol): 1675 (vs), 1586 (w), 1569 (w), 1520 (w), 1225 (w), 1189 (w), 1160 (w), 1112 (w), 1093 (s), 1013 (m), 981 (s), 935 (m), 823 (s), 750 (s), 697 (vs), 616 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.89–7.05 (complex multiplets, 15 H), 4.92 (s, 5 H).

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Registry No. [PPN]·**1**, 97112-44-2; [PPN]·**2**, 112068-74-3; K[18-crown-6]·**3a**, 85369-56-8; [Et_4N]·**3b**, 85369-55-7; [Et_4N]·**4a**, 85369-58-0; K[18-crown-6]·**5a**, 85369-62-6; [Et_4N]·**5b**, 85369-64-8; [PPN]·**5b**, 85369-65-9; **6**, 112043-73-9; **7**, 106712-24-7; K[18-crown-6]·**8**, 85369-67-1; **9**, 112022-79-4; **10**, 85356-06-5; **12**, 103731-57-3; **13**, 103731-58-4; **14**, 112043-74-0; **15**, 112043-75-1; K[18-crown-6][$Mn(CO)_5$], 85356-08-7; [η^5-$C_5Me_5)Ir(CO)_2$, 32660-96-1; $Re_2(CO)_{10}$, 14285-68-8; (η_5-$C_5Me_5)Rh(CO)(PMe_3)$, 80182-11-2; (η^5-$C_5Me_5)Rh(CO)_2$, 32627-01-3; (η^5-$C_5H_5)Ir(CO)$-

(PPh$_3$), 32612-68-3; (η^5-C$_5$H$_5$)Rh(CO)(PPh$_3$), 12203-88-2; (η^5-C$_5$H$_5$)Co(CO)(PPh$_3$), 12203-85-9; *M*-FC$_6$H$_4$C(Cl)NOH, 58606-42-1; *p*-FC$_6$H$_4$C(Cl)NOH, 42202-95-9; *p*-ClC$_6$H$_4$C(Cl)NOH, 28123-63-9; *M*-FC$_6$H$_4$C(H)NOH, 458-02-6; *p*-FC$_6$H$_4$C(H)NOH, 459-23-4; *p*-ClC$_6$H$_4$C(H)NOH, 3848-36-0; C$_6$H$_5$C(Cl)NOH, 698-16-8; 2,4,6-Me$_3$C$_6$H$_2$CNO, 2904-57-6.

Supplementary Material Available: Listings of parameters for hydrogen atoms and for atoms refined as members of rigid groups, anisotropic thermal parameters, and complete listings of interatomic distances and angles for PPN·**5b** and **9** (12 pages); listings of structure factors for PPN·**5** and **9** (47 pages). Ordering information is given on any current masthead page.

Formation of η^2-Side-Bonded Aryl Nitrile Complexes from 4-Metallaisoxazolin-5-one Species and Their Application in the Thermal and Photochemical Activation of C–H Bonds

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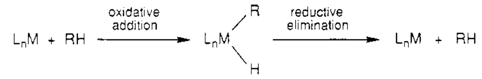
Thermolysis of the 4-metallaisoxazolin-5-one metallacycles (η^5-C$_5$H$_5$)(PPh$_3$)Ir{η^2-(Ar)NOC(=O)-} (Ar = *p*-ClC$_6$H$_4$ (**1a**), *p*-FC$_6$H$_4$ (**1b**)) at 110 °C for 24 h in toluene leads to the novel side-bonded nitrile complexes (η^5-C$_5$H$_5$)(PPh$_3$)Ir(η^2-NCAr) (Ar = *p*-ClC$_6$H$_4$ (**7a**), *p*-FC$_6$H$_4$ (**7b**)) by an intramolecular process involving loss of CO$_2$ from **1a** and **1b**. The stability of **7a** and **7b** and their mode of formation suggest that these complexes are best described as the product of oxidative addition of an Ir(I) metal fragment into a CN triple bond. The single-crystal X-ray diffraction study of **7a** is reported and the structure discussed. Crystallographic data for **7a**: 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, and Z = 8. Thermolysis, in the dark, of the metallacycle (η^5-C$_5$Me$_5$)(CO)Ir{η^2-C(*p*-ClC$_6$H$_4$)NOC(=O)-} (**9**) in benzene at 50 °C for 5 weeks leads to the C–H activation product (η^5-C$_5$Me$_5$)Ir(CO)(H)(C$_6$H$_5$) (**11**) in 90% yield by ^{1}H NMR. The dimer [(η^5-C$_5$Me$_5$)Ir(μ-CO)]$_2$ (**13**) was also identified in 8.6% yield. When **9** was warmed in cyclohexane for 5 weeks under the same conditions, the iridium cyclohexyl hydride (η^5-C$_5$Me$_5$)Ir(CO)(H)(C$_6$H$_{11}$) (**14**) was obtained in 3% yield and dimer **13** was obtained in 65% yield. These thermal reactions are shown to proceed via the side-bonded nitrile intermediate (η^5-C$_5$Me$_5$)(CO)Ir(η^2-NCC$_6$H$_4$Cl) (**16**) which has been isolated, characterized, and shown to independently activate benzene C–H bonds at 50 °C. A single-crystal X-ray diffraction study of **16** is reported and the crystal structure discussed. Crystallographic data for **16**: space group *P*2$_1$/*a*; a = 7.859 (2) Å, b = 20.010 (4) Å, c = 11.721 (2) Å, β = 108.757 (4)°, V = 1745 Å^3, and Z = 4. Complexes **16** and **9** could be readily decomposed under mild photochemical conditions in benzene and cyclohexane to yield the iridium phenylhydride product **11** and the iridium cyclohexylhydride product **14** in high yield. Thermolysis of (η^5-C$_5$Me$_5$)(PMe$_3$)Rh{η^2-C(*p*-FC$_6$H$_4$)NOC(=O)-} (**10**) for 3 days in benzene at 50 °C leads to (η^5-C$_5$Me$_5$)(PMe$_3$)Rh(η^2-NCC$_6$H$_4$F) (**18**) in 80% yield and to (η^5-C$_5$Me$_5$)(PMe$_3$)Rh(C$_6$H$_5$)(H) in 13% yield. When the reaction was carried out in toluene under these conditions, **18** was obtained in 60% yield and the C–H activation products (η^5-C$_5$Me$_5$)(PMe$_3$)Rh(H)(*p*-C$_6$H$_4$CH$_3$) and (η^5-C$_5$Me$_5$)(PMe$_3$)Rh(H)(*m*-C$_6$H$_4$CH$_3$) were obtained in 2% and 4% yields, respectively.

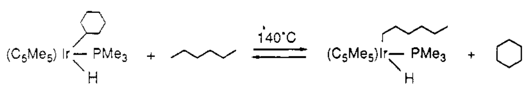
Introduction

Coordinatively unsaturated 16-electron metal species are believed to be the active intermediates responsible for the remarkable intermolecular activation of a variety of saturated and aromatic hydrocarbons.[1–6] The success of these reactions with typically unreactive carbon–hydrogen bonds of hydrocarbons must be attributed to the unique structural and electronic features[7] of these metal-containing moieties that stabilize the intermolecular oxidative addition product with respect to reductive elimination of hydrocarbon from the substituted metal center.[8] As has been

Scheme I



Scheme II



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