(PPh_3), 32612-68-3; $(\eta^5\text{-}C_5H_5)Rh(CO)(PPh_3)$, 12203-88-2; $(\eta^5\text{-}C_5H_5)Co(CO)(PPh_3)$, 12203-85-9; $M\text{-}FC_6H_4C(Cl)NOH$, 58606-42-1; $p\text{-}FC_6H_4C(Cl)NOH$, 42202-95-9; $p\text{-}ClC_6H_4C(Cl)NOH$, 28123-63-9; $M\text{-}FC_6H_4C(H)NOH$, 458-02-6; $p\text{-}FC_6H_4C(H)NOH$, 459-23-4; $p\text{-}ClC_6H_4C(H)NOH$, 3848-36-0; $C_6H_5C(Cl)NOH$, 698-16-8; 2,4,6-$Me_3C_6H_2CNO$, 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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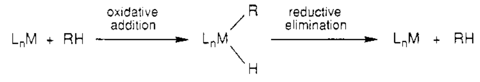
Thermolysis of the 4-metallaisoxazolin-5-one metallacycles $(\eta^5\text{-}C_5H_5)(PPh_3)Ir\{\eta^2\text{-}(Ar)NOC({=}O)\text{–}\}$ (Ar = $p\text{-}ClC_6H_4$ (**1a**), $p\text{-}FC_6H_4$ (**1b**)) at 110 °C for 24 h in toluene leads to the novel side-bonded nitrile complexes $(\eta^5\text{-}C_5H_5)(PPh_3)Ir(\eta^2\text{-}NCAr)$ (Ar = $p\text{-}ClC_6H_4$ (**7a**), $p\text{-}FC_6H_4$ (**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 $(\eta^5\text{-}C_5Me_5)(CO)Ir\{\eta^2\text{-}C(p\text{-}ClC_6H_4)NOC({=}O)\text{–}\}$ (**9**) in benzene at 50 °C for 5 weeks leads to the C–H activation product $(\eta^5\text{-}C_5Me_5)Ir(CO)(H)(C_6H_5)$ (**11**) in 90% yield by ^1H NMR. The dimer $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}CO)]_2$ (**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 $(\eta^5\text{-}C_5Me_5)Ir(CO)(H)(C_6H_{11})$ (**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 $(\eta^5\text{-}C_5Me_5)(CO)Ir(\eta^2\text{-}NCC_6H_4Cl)$ (**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 $P2_1/a$; $a = 7.859$ (2) Å, $b = 20.010$ (4) Å, $c = 11.721$ (2) Å, $\beta = 108.757$ (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 $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh\{\eta^2\text{-}C(p\text{-}FC_6H_4)NOC({=}O)\text{–}\}$ (**10**) for 3 days in benzene at 50 °C leads to $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(\eta^2\text{-}NCC_6H_4F)$ (**18**) in 80% yield and to $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(C_6H_5)(H)$ 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 $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(H)(p\text{-}C_6H_4CH_3)$ and $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(H)(m\text{-}C_6H_4CH_3)$ were obtained in 2% and 4% yields, respectively.

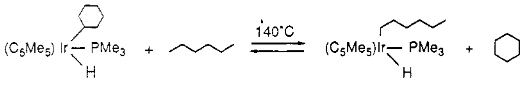
Introduction

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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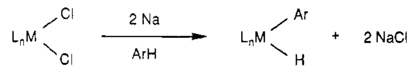
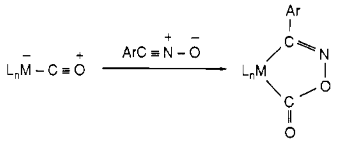
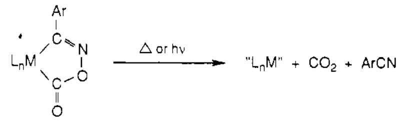
Scheme III



Scheme IV



Scheme V



pointed out in recent review papers[7a,9] a number of favorable factors are necessary to allow fragments such as "(η^5-C_5Me_5)Ir(PMe_3)", "(η^5-C_5Me_5)Ir(CO)", and "(η^5-C_5H_5)Re(PMe_3)$_2$" to insert into C–H bonds. These include (i) the strength of the M–C and M–H bonds in the oxidative addition product,[1e,7a,9] (ii) a sterically uncongested metal center that appears to promote intermolecular C–H activation[7a,9] (as opposed to the more common intramolecular cyclometallation[10]), and (iii) suitable acceptor and donor orbitals that can interact with the $\sigma_{\text{C-H}}$ and $\sigma^*_{\text{C-H}}$ orbitals of the alkane.[7a,9b] Another obvious factor is that the lower the thermodynamic stability of the metal fragment affecting C–H activation, the more stable the resulting alkyl or aryl metal hydride will be with respect to reductive elimination, since such a process would necessarily generate the reactive metal species initially present (Scheme I).[7a,9a] Furthermore, it would be expected that the generation of such a highly energetic metal species from a thermodynamically stable metal complex would require a high activation energy if the reactive species were produced by reductive elimination or ligand dissociation reactions. Consequently, the in situ generation of reactive metal species has been achieved photochemically by reductive elimination of dihydrogen,[1a,b,4,5] dissociation of carbon monoxide,[2,6] and more recently dissociation of trimethylphosphine[1c] from low-valent transition-metal complexes in hydrocarbon solutions. Reactive species capable of C–H activation have also been shown to be thermally accessible as demonstrated by the hydrocarbon exchange equilibria mediated by the metal fragment (η^5-C_5Me_5)Ir(PMe_3) which, in turn, is generated by thermally activated reductive elimination of iridium hydrocarbyl hydrides (Scheme II).[1d,e] There are a number of other examples of thermal C–H bond activation based upon the reductive elimination of alkyl or aryl metal hydrides to generate reactive metal species which then proceed to oxidatively add C–H bonds of other hydrocarbons.[11] Since these reactions require as one component a metal center which has already undergone C–H activation, they constitute hydrocarbon exchange reactions. Reactive metal fragments capable of affecting C–H bond activation have also been generated by the reduction of metal dichloro complexes by group I metals in arene solvents (Scheme III).[11b–d,12] The aromatization of cyclic hydrocarbons in the presence of the hydrogen acceptor 3,3-dimethyl-1-butene catalyzed by the cationic iridium complex $[IrH_2S_2L_2]^+$ (S = coordinating solvent; L = phosphine ligand)[13a,b] and ReH_7L_2 (L = phosphine ligand)[13c] are further examples of C–H activation by transition-metal complexes under mild thermal conditions. Werner et al.[14] have very recently reported the very interesting thermolytic activation of arene C–H bonds using [ClIr($PiPr_3$)$_2$] prepared in situ.

In order for a coordinatively and electronically saturated transition-metal complex to achieve C–H bond activation under mild thermal or photochemical conditions, the activation energy required for production of the reactive metal intermediate must be reduced as much as possible. This can be achieved by reducing the thermodynamic stability of the initial metal complex with respect to the reactive metal species released. In this paper we report the thermal and photochemical decomposition of metallacycles generated by the 1,3-dipolar cycloaddition of aryl nitrile *N*-oxides to the M–CO bond of low-valent metal carbonyl complexes of rhodium and iridium.[16b] Thermal and photochemical decomposition of these cycloadducts in hydrocarbon solvents under mild conditions results in the activation of the solvent C–H bonds and, in addition, has led to the isolation of a novel class of side-bonded nitrile complexes that serve as intermediates in the C–H activation sequence. Initial results describing the decomposition of these metallacycles has already been reported.[15]

Results and Discussion

The synthesis of five-membered 4-metallaisoxazolin-5-one metallacycles formed by the 1,3-dipolar cycloaddition of aryl nitrile *N*-oxides to the M–CO bond of low-valent carbonyl complexes (Scheme IV) have recently been communicated.[16a] We have now extended this reaction to include a variety of low-valent metal carbonyl complexes of rhodium and iridium, and a full report detailing the syntheses of these metallacycles will be published shortly.[16b]

It was immediately apparent that these metallacycles should provide a facile route toward the liberation of 16-electron, coordinatively unsaturated metal fragments since the loss of CO_2 and the nitrile ligand from the five-membered cycle would provide a thermodynamic driving force. By selecting the appropriate metallacycle, we hoped to generate metal fragments such as "(η^5-C_5Me_5)Ir(CO)" and "(η^5-C_5Me_5)M(PMe_3)" (M = Ir, Rh) under mild thermal or photochemical conditions (Scheme V). The factors influencing the stability of these metallacycles have been discussed in detail elsewhere.[16b] However, it is apparent that the nature of the metal center (whether first-, second-, or third-row transition metal) had a dominant influence

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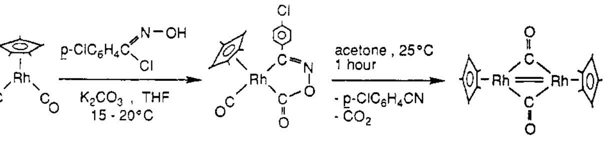
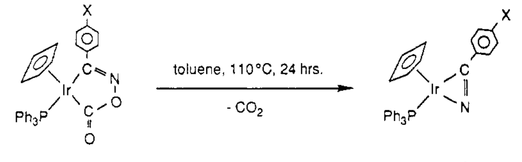
Scheme VI



Scheme VII



1a, X=Cl
1b, X=F

7a, X=Cl
7b, X=F

upon the relative stabilities of these complexes. For example, the metallacycles (η^5-C_5H_5)(PPh_3)Ir{η^2-C(Ar)NOC(=O)-} (Ar = p-ClC_6H_4 (**1a**), p-FC_6H_4 (**1b**),[16b] (η^5-C_5H_5)(PPh_3)Rh{η^2-C(p-FC_6H_4)NOC(=O)-} (**2**),[16b] and (η^5-C_5H_5)(PPh_3)Co{η^2-C(p-ClC_6H_4)NOC(=O)-} (**3**)[16b] show a wide range of thermal stabilities in solution; **1a** and **1b** decompose at 110 °C over 24 h, **2** decomposes at room temperature over several hours, and orange solutions of **3** turn dark instantaneously above 20 °C. These stabilities reflect the relative metal-carbon bond strength of first-, second-, and third-row transition metals.[17] Another important factor influencing the stability of these metallacycles was the degree of π-back-bonding from the metal center to π^*-orbitals of the chelate ligand. A greater degree of π-back-bonding increased the stability of the metallacycle. Consequently, increasing the electron density on the metal, by substitution of stronger σ-donor ligands, increased the stability of the metallacycles. Initial results revealed that the rhodium metallacycle (η^5-C_5Me_5)(CO)Rh{η^2-C(p-ClC_6H_4)NOC(=O)-} (**4**), obtained by reaction of p-chlorobenzonitrile N-oxide and (η^5-C_5Me_5)Rh$(CO)_2$ (**5**), was thermally labile in solution, rapidly decomposing to yield the known dimer [(η^5-C_5Me_5)Rh(μ-CO)$_2$]$_2$ (**6**) (Scheme VI).[18] Compound **6** formally results from the loss of CO_2 and p-ClC_6H_4CN from **4** to generate the presumed four-coordinate, 16-electron metal fragment which apparently dimerizes. The rhodium dimer has also been obtained by reaction of (η^5-C_5Me_5)Rh$(CO)_2$ (**5**) with trimethylamine N-oxide[19] and also by photolysis of **5** in cyclohexane at 298 K.[20] The failure to observe C-H activation products during the latter reactions is probably a result of the instability of rhodium alkyl hydrides at the temperatures employed in these reactions.[20,21]

Thermal Decomposition of (η^5-C_5H_5)(PPh_3)Ir{η^2-C(Ar)NOC(=O)-} (Ar = p-ClC_6H_4 (1a), p-FC_6H_4 (1b)). The metallacycles **1a** and **1b** exhibited remarkable thermal stabilities when compared to other similar metallacycles which we had synthesized[16] and only slowly decomposed over a period of 24 h at 110 °C in toluene. When the decomposition of **1a** or **1b** was monitored by $^{31}P\{^1H\}$ NMR, the resonances at -2.22 (**1a**) or -2.09 ppm (**1b**) were replaced by new resonances at 16.56 and 16.29 ppm, respectively, in essentially quantitative yield due to products **7a** and **7b** (Scheme VII). The ^1H NMR of the products did not reveal hydride resonances upfield from tetramethylsilane that might have been present due to C-H activation of the solvent or intramolecular cyclometalation by the metal fragment "(η^5-C_5H_5)Ir(PPh_3)". In view of the ortho metalation products obtained when the "(η^5-C_5Me_5)Ir(PPh_3)" is generated by the photolysis of (η^5-C_5Me_5)Ir(PPh_3)$(H)_2$[1b] an intramolecular cyclometalation reaction would have been expected. The infrared spectra of **7a** and **7b** showed unexpected absorptions at 1758 and 1756 cm^{-1}, respectively, which were difficult to reconcile with any expected structure. In order to establish the nature of the thermolysis products of **1a** and **1b**, crystals of **7a** were grown and an X-ray diffraction study was undertaken which is discussed below. The structure obtained was that of the side-bonded nitrile complex (η^5-C_5H_5)(PPh_3)Ir(η^2-NCC_6H_4Cl) (**7a**). An ORTEP projection of **7a** is shown in Figure 1. All IR, ^1H NMR, and ^{31}P NMR spectra and elemental analyses were in agreement with this structure. Compound **7b** also was characterized by IR and NMR spectra coupled with elemental analyses and formulated as (η^5-C_5H_5)(PPh_3)Ir(η^2-NCC_6H_4F) (**7b**). In order to establish whether formation of the side-bonded nitrile complexes **7a** and **7b** occurred by an intramolecular mechanism in which CO_2 was extruded from the metallacycles **1a** and **1b** to directly yield the coordinated nitrile complexes or if an intermolecular process was involved in which loss of CO_2 and nitrile ligand generated the 16-electron fragment "CpIr(PPh_3)" which then coordinated the free nitrile, **1b** was decomposed in the presence of a 20-fold excess of p-ClC_6H_4CN (Scheme VIII). Both ^{31}P and ^{19}F NMR identified **7b** as the predominant product (80% yield by NMR), and no resonance corresponding to **7a** was observed in the ^{31}P NMR of the products. The result of this crossover experiment indicated that no nitrile exchange had occurred and formation of **7a** and **7b** from the corresponding metallacycles **1a** and **1b** occurred by an intramolecular process. This result was not surprising in view of our failure to observe C-H activation products due to intramolecular cyclometalation or due to intermolecular solvent activation. If the metal fragment "(η^5-C_5H_5)Ir(PPh_3)" were generated in solution from **1a** or **1b**, some

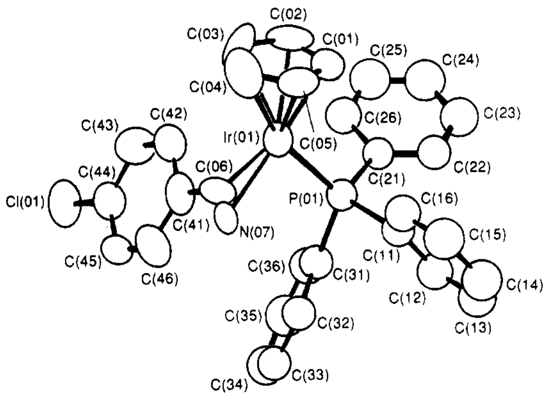
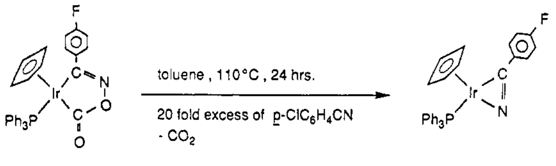


Figure 1. ORTEP projection of the side-bonded nitrile complex (η^5-C_5H_5)(PPh_3)Ir(η^2-NCC_6H_4Cl) (**7a**). Hydrogen atoms have been omitted for clarity.

Scheme VIII



1b

7b

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Table I. Selected Interatomic Distances (Å) and Angles (deg) for Side-Bonded Nitrile Complexes 7a and 16

	7a	16
Bond Distances		
Ir(01)–C(06)	2.105 (23)	2.040 (8)
Ir(01)–N(07)	2.174 (15)	2.185 (5)
Ir(01)–P(01)	2.225 (5)	
Ir(01)–C(01)	2.213 (21)	2.237 (9)
Ir(01)–C(02)	2.245 (22)	2.223 (8)
Ir(01)–C(03)	2.259 (24)	2.267 (8)
Ir(01)–C(04)	2.247 (25)	2.252 (9)
Ir(01)–C(05)	2.262 (26)	2.274 (9)
Ir(01)–C(08)		1.829 (9)
C(06)–N(07)	1.231 (28)	1.209 (11)
C(08)–O(09)		1.178 (11)
C(06)–C(41)		1.488 (11)
Cl(01)–C(44)		1.745 (8)
Bond Angles		
C(06)–Ir(01)–N(07)	33.4 (11)	33.0 (3)
C(06)–Ir(01)–P(01)	91.1 (6)	
C(06)–Ir(01)–C(08)		89.3 (3)
N(07)–Ir(01)–P(01)	91.9 (5)	
N(07)–Ir(01)–C(08)		92.7 (3)
Ir(01)–C(08)–O(09)		179.0 (7)
Ir(01)–C(06)–N(07)	76.4 (14)	80.1 (6)
Ir(01)–N(07)–C(06)	70.2 (12)	66.9 (5)

Table II. Positional and Equivalent Isotropic Thermal Parameters for 7a and 16

7a

atom	x	y	z	10^4U(eq),[a] Å^2
Ir(01)	0.04974 (8)	0.07803 (5)	0.16911 (2)	508 (4)
P(01)	0.0477 (5)	0.0327 (3)	0.1052 (1)	484 (28)
Cl(01)	−0.6219 (7)	−0.1027 (5)	0.2030 (2)	1065 (57)
C(06)	−0.0810 (27)	−0.0266 (15)	0.1844 (6)	635 (154)
N(07)	0.0214 (22)	−0.0644 (11)	0.1901 (6)	714 (131)
C(01)	0.1583 (31)	0.2096 (15)	0.1646 (8)	890 (196)
C(02)	0.0263 (37)	0.2326 (15)	0.1782 (13)	1201 (262)
C(03)	0.0062 (35)	0.1897 (23)	0.2150 (12)	1081 (256)
C(04)	0.1195 (41)	0.1490 (22)	0.2250 (9)	1052 (245)
C(05)	0.2095 (25)	0.1602 (17)	0.1967 (10)	811 (186)
C(11)	0.1981 (20)	0.0095 (13)	0.0819 (6)	558 (126)
C(12)	0.2084 (22)	−0.0330 (14)	0.0442 (6)	621 (137)
C(13)	0.3290 (30)	−0.0500 (16)	0.0266 (8)	794 (179)
C(14)	0.4363 (29)	−0.0324 (18)	0.0489 (9)	924 (210)
C(15)	0.4252 (23)	0.0077 (19)	0.0834 (9)	829 (189)
C(16)	0.3113 (21)	0.0230 (14)	0.1022 (7)	666 (153)
C(21)	−0.0239 (20)	0.1194 (12)	0.0713 (6)	551 (129)
C(22)	0.0253 (21)	0.1479 (14)	0.0354 (6)	640 (140)
C(23)	−0.0405 (26)	0.2169 (16)	0.0136 (7)	798 (170)
C(24)	−0.1415 (32)	0.2572 (18)	0.0269 (7)	949 (196)
C(25)	−0.1943 (29)	0.2257 (21)	0.0616 (7)	1133 (223)
C(26)	−0.1311 (24)	0.1593 (16)	0.0842 (6)	713 (154)
C(31)	−0.0387 (21)	−0.0755 (13)	0.0935 (6)	561 (117)
C(32)	0.0180 (21)	−0.1600 (14)	0.1082 (7)	669 (146)
C(33)	−0.0465 (25)	−0.2421 (15)	0.1048 (7)	751 (155)
C(34)	−0.1618 (33)	−0.2421 (18)	0.0881 (9)	989 (216)
C(35)	−0.2215 (24)	−0.1637 (23)	0.0737 (8)	929 (205)
C(36)	−0.1554 (21)	−0.0779 (15)	0.0774 (7)	695 (147)
C(41)	−0.2059 (23)	−0.0427 (16)	0.1888 (6)	571 (137)
C(42)	−0.2935 (28)	0.0277 (18)	0.1913 (7)	810 (180)
C(43)	−0.4142 (24)	0.0093 (16)	0.1964 (7)	720 (165)
C(44)	−0.4642 (22)	−0.0830 (16)	0.1982 (7)	704 (151)
C(45)	−0.3735 (32)	−0.1544 (16)	0.1963 (8)	925 (203)
C(46)	−0.2491 (27)	−0.1341 (17)	0.1924 (8)	874 (196)

16

atom	x	y	z	U^2,[b] Å^2
Ir(01)	0.35830 (4)	0.39183 (1)	0.79630 (3)	0.018
Cl(01)	0.4160 (3)	0.7656 (1)	0.6954 (2)	0.041
C(01)	0.1559 (10)	0.3768 (4)	0.8914 (9)	0.028
C(02)	0.2239 (10)	0.3117 (4)	0.8673 (8)	0.024
C(03)	0.1694 (10)	0.3034 (4)	0.7416 (8)	0.026
C(04)	0.0756 (11)	0.3636 (4)	0.6868 (8)	0.026
C(05)	0.0640 (11)	0.4070 (4)	0.7781 (9)	0.029
C(06)	0.4154 (11)	0.4672 (4)	0.6973 (8)	0.025
N(07)	0.4499 (9)	0.4195 (4)	0.6454 (7)	0.031
C(08)	0.5835 (11)	0.4005 (3)	0.9056 (7)	0.021
O(09)	0.7290 (8)	0.4069 (3)	0.9750 (5)	0.031
C(10)	0.1727 (13)	0.4027 (5)	1.0142 (10)	0.039
C(20)	0.3133 (11)	0.2618 (4)	0.9625 (8)	0.032
C(30)	0.1941 (12)	0.2421 (4)	0.6725 (10)	0.039
C(41)	0.4147 (10)	0.5416 (4)	0.6944 (7)	0.024
C(42)	0.4915 (11)	0.5762 (4)	0.6211 (7)	0.025
C(43)	0.4928 (11)	0.6450 (4)	0.6215 (7)	0.028
C(44)	0.4151 (11)	0.6784 (4)	0.6933 (8)	0.028
C(45)	0.3383 (11)	0.6450 (4)	0.7690 (9)	0.031
C(46)	0.3405 (11)	0.5755 (4)	0.7679 (9)	0.030
C(50)	−0.0433 (12)	0.4714 (4)	0.7620 (11)	0.041
C(40)	−0.0015 (12)	0.3771 (5)	0.5494 (9)	0.036 (2)*

[a] $U(\mathrm{eq}) = [1/(6\pi^2)]\sum\beta(ij)a(i)a(j)$. [b] Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. The asterisk denotes an atom refined isotropically. Other isotropic values are $[1/(8\pi^2)]$ times the "equivalent B value" for an anisotropic atom, as defined by: Hamilton, W. C. *Acta Crystallogr.* *12*, 609–610.

C–H oxidative addition products would be expected. The failure to observe any direct nitrile exchange between **7b** and p-ClC_6H_4CN (Scheme VIII) is also an indication of the relatively high kinetic stability of these side-bonded nitrile complexes. The IR spectra of **7a** and **7b** exhibit CN stretching frequencies at 1758 and 1756 cm^{-1}, respectively, a decrease of 472 and 468 cm^{-1} from the CN stretch of the corresponding free nitriles. These large reductions of the CN stretching frequencies suggest a decrease in the CN bond order. Similar large reductions of the CN stretching frequencies have been observed in other complexes believed to contain side-bonded nitrile ligands[22] as opposed to the more common mode of nitrile coordination to a metal center which occurs by σ-bonding through the nitrogen lone pair.[23] The stability of **7a** and **7b** and their mode of formation suggest that these complexes are perhaps best described formally as the products of the oxidative addition of an Ir(I) 16-electron fragment into the CN triple bonds of the corresponding aryl nitrile to generate formal $\overline{\mathrm{Ir^{III}{—}C{=}N}}$ metallacycles, rather than simple π-complexes of the nitriles to a metal center. In contrast, the nitrile ligand of the side-bonded nitrile complex $(PPh_3)_2Pt(\pi\text{-}CF_3CN)$[22a] is readily displaced by CO and diphenylacetylene at room temperature. Prior to the present work, the only side-bonded nitrile complexes reported which showed chemical properties similar to those of **7a** and **7b** were the molybdenocene nitrile complexes $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}NCR)$ (R = CH_3, CF_3, Ph) obtained by generating molybdenocene in situ in the presence of the corresponding nitrile.[22e] The tungsten acetonitrile analogue $(\eta^5\text{-}C_5H_5)_2W(\eta^2\text{-}NCCH_3)$ has also been characterized.[22f] At the time we initially communicated our results on the characterization of **7a** and **7b** and the X-ray crystal structure of **7a**[15a] there were no structurally characterized η^2-nitrile complexes. Recently, the X-ray crystal structure of $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}NCCH_3)$ (**8**) was reported,[24] confirming the η^2-coordination of the acetonitrile. The structural features of **8** are very similar to those of the side-bonded

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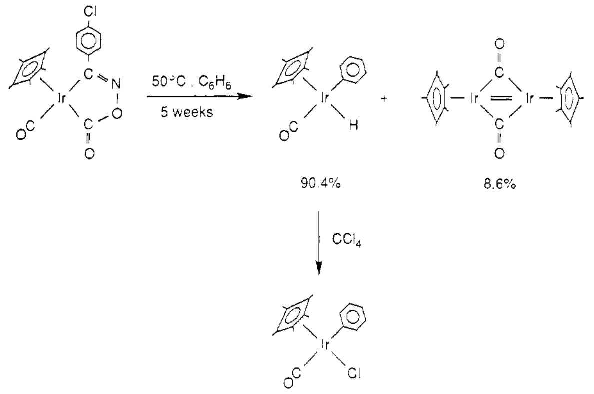
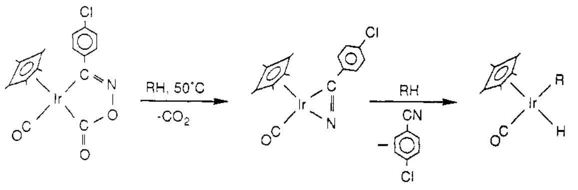
Scheme IX



nitrile complex **7a** and $(\eta^5\text{-}C_5H_5)(CO)Ir(\eta^2\text{-}NCC_6H_4Cl)$ reported here and elsewhere.[15a]

X-ray Crystal Structure of $(\eta^5\text{-}C_5H_5)(PPh_3)Ir(\eta^2\text{-}NCC_6H_4Cl)$ (7a). Yellow crystals of **7a** were grown from an ether solution at room temperature; after a suitable crystal was selected, an X-ray diffraction study was undertaken. Relevant bond angles and bond distances are given in Table I; positional and thermal parameters are given in Table II. The Ir–C(6) bond length is 2.11 (2) Å, which is the expected length for an Ir(III)–C bond;[1e,25] the Ir–N bond distance of 2.17 (2) Å represents a long Ir–N single bond though it is within the range for Ir–N single bonds.[26] The C(6)–N bond distance is 1.23 (3) Å, which represents a lengthening of 0.08 Å relative to that of free nitriles. A number of η^2-coordinated acetylene complexes have been structurally characterized and are observed to undergo large reductions in their C–C stretching frequencies accompanied by lengthening of the C–C bond length.[24] The average increase in the C–C bond length for η^2-coordinated acetylenes is 0.08 Å; this is the same lengthening observed for the C–N distance of **7a**, suggesting the nitriles undergo a similar reduction in bond order on coordination. The C–N bond distance reported for the side-bonded nitrile complex $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}NCCH_3)$ (**8**)[24] was 1.20 Å which compares to the C–N bond distance of **7a** (1.23 Å). Furthermore, the N–C–C bond angle of the coordinated nitrile of **7a** was reduced from 180° to 136°, and this is nearly equal to the value of the N–C–C angle (138°) reported for compound **8**.[24] Consequently, coordination of the nitrile ligand in a side-bonded fashion in complexes **7a** and **8**[24] leads to comparable lengthening in the C–N bond distance as well as very similar deformations in the N–C–C bond angle, suggesting a similar metal to coordinated nitrile bonding interaction which can best be described by η^2-coordination of the nitrile to generate a formal $\overline{M{-}C{=}N}$ metallacycle.[15a,24]

Scheme X



Thermal C–H Bond Activation by Precursor 4-Metallaisoxazolin-5-one Derivatives. The iridium and rhodium metallacycles, $(\eta^5\text{-}C_5Me_5)(CO)Ir\{\eta^2\text{-}C(p\text{-}ClC_6H_4)NOC({=}O)\text{-}\}$ (**9**) and $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh\{\eta^2\text{-}C(p\text{-}FC_6H_4)NOC({=}O)\text{-}\}$ (**10**), would respectively release the 16-electron four-coordinate metal fragments "$(\eta^5\text{-}C_5Me_5)Ir(CO)$"[2] and "$(\eta^5\text{-}C_5Me_5)Rh(PMe_3)$"[1f,3,4] when decomposed in accord with Scheme V. These species are believed to be the reactive intermediates responsible for the activation of hydrocarbons when generated photolytically from $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ and $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(H)_2$.[1f,3,4] When **9** was maintained in benzene at 50 °C in the dark, the metallacycle dissolved after about 4 days, and after 35 days, the reaction was complete; a single hydride resonance was observed in the ^1H NMR spectrum of the product attributed to $(\eta^5\text{-}C_5Me_5)Ir(CO)(H)(C_6H_5)$[2a] (**11**) formed by the oxidative addition of the metal fragment "$(\eta^5\text{-}C_5Me_5)Ir(CO)$"[2] into the C–H bonds of benzene. Addition of CCl_4 converted **11** into the known $(\eta^5\text{-}C_5Me_5)Ir(CO)(Cl)(C_6H_5)$[2a,28] (**12**) in 90.4% yield. In addition to the phenyl hydride product (**11**), the known dimer $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}CO)]_2$ (**13**)[29] was identified in 8.6% yield by its ^1H NMR resonance at 1.58 ppm in C_6D_6 (Scheme IX). Warming **9** in cyclohexane under the same conditions for 5 weeks yielded predominantly dimer **13**[29] in 65% yield. The known cyclohexyl hydride complex $(\eta^5\text{-}C_5Me_5)Ir(CO)(H)(C_6H_{11})$ (**14**)[2a] was observed in low yield and addition of CCl_4 converted **14** to $(\eta^5\text{-}C_5Me_5)Ir(CO)(Cl)(C_6H_{11})$[2a] (**15**) in 3% yield based on starting metallacycle **9**. When the thermolysis of **9** was carried out in deuteriated benzene and the reaction monitored by ^1H NMR, the resonances due to **9** at 7.38, 7.09, and 1.22 ppm (Figure 2) were slowly replaced by a new set of resonances at 7.72, 7.01, and 1.69 ppm. This set of resonances eventually decreases in intensity due to the formation of $(\eta^5\text{-}C_5Me_5)Ir(CO)(D)(C_6D_5)$ (**17**) identified by its resonance at 1.62 ppm. A multiplet centered at 6.60 ppm was the only resonance in the phenyl region of the ^1H NMR spectrum of the products and corresponded to free *p*-chlorobenzonitrile. When the reaction was carried out in deuteriated cyclohexane, the same intermediate resonances were observed, suggesting that a common intermediate was involved in the thermolysis of **9** in both benzene and cyclohexane. In order to isolate the intermediate, a THF solution of **9** was maintained at 50 °C for 14 h in the dark. The pale yellow solution of **9** turned yellow-orange in color. When the solvent was removed in vacuo and the residue was extracted with pentane, a yellow solution was obtained, which on cooling to −20 °C afforded yellow crystals of compound **16** in 66% yield. The IR spectrum of **16** gave an absorption at 1781 cm^{-1}, suggesting that the complex was the side-bonded nitrile complex $(\eta^5\text{-}C_5Me_5)Ir(\eta^2\text{-}NCC_6H_4Cl)(CO)$ (**16**). Both the ^1H NMR and elemental analyses were in agreement with this formulation and the structure was confirmed by an X-ray crystallographic study described below. An ORTEP projection of **16** is shown in Figure 3. Crystals of **16** could be handled in air and were stable when kept under N_2 for extended periods of time.

The results indicated that activation of benzene or cyclohexane does not occur by the direct release of the metal fragment "$(\eta^5\text{-}C_5Me_5)Ir(CO)$"[2a] by complex **9**. Alterna-

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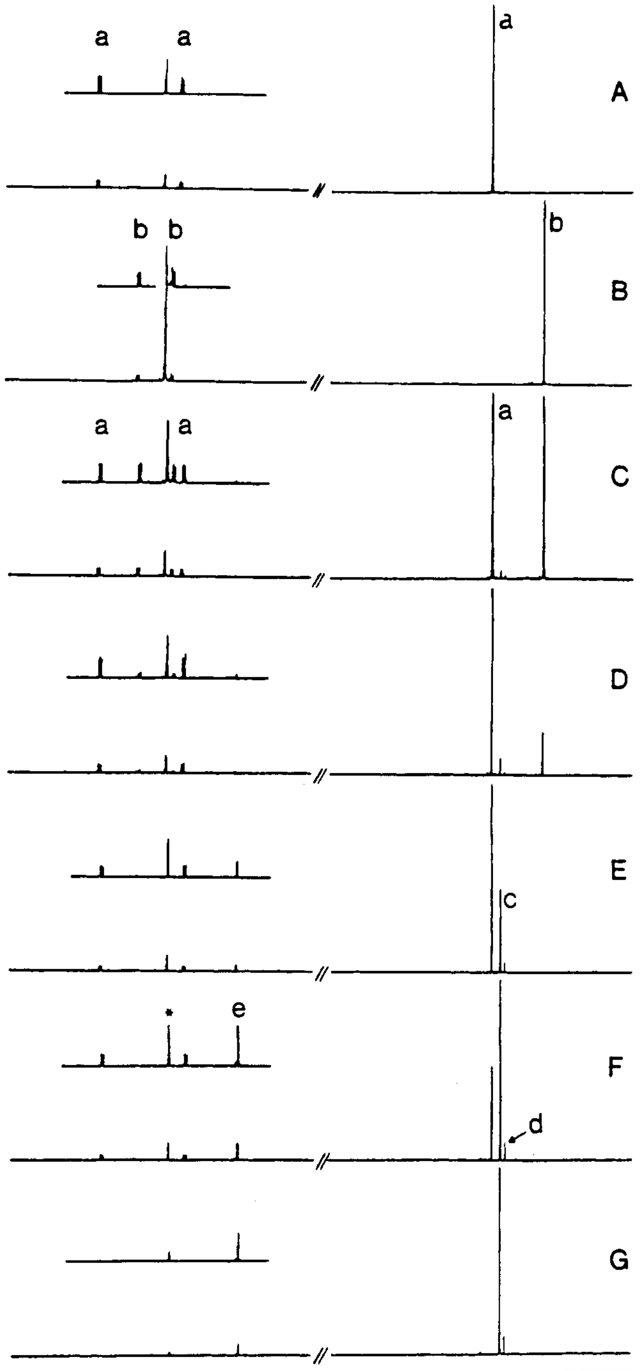


Figure 2. ^{1}H NMR spectra (500 MHz) showing the conversion of (η^5-C_5Me_5)(CO)Ir{η^2-C(p-ClC_6H_4)NOC(=O)-} (**9**) to (η^5-C_5Me_5)Ir(CO)(D)(C_6D_5) (**17**) via the side-bonded nitrile intermediate (η^5-C_5Me_5)(CO)Ir(η^2-NCC_6H_4Cl) (**16**) in C_6D_6 at 50 °C: (A) spectrum of **16** in C_6D_6 for comparison; (B) spectrum of **9** in C_6D_6; (C) after 1 day; (D) after 5 days; (E) after 22 days; (F) after 30 days; (G) after 36 days; (a) resonances due to **16**; (b) resonances due to **9**; (c) resonances due to **17**; (d) resonances due to [(η^5-C_5Me_5)Ir(μ-CO)]$_2$ (**13**); (e) resonances due to free p-chlorobenzonitrile; (*) residual protons in C_6D_6.

tively, a labile side-bonded nitrile complex, **16**, is formed from metallacycle **9** which under the reaction conditions very slowly loses its nitrile ligand and oxidatively adds solvent C–H bonds (Scheme X). The relative ease with which the p-ClC_6H_4CN ligand is lost from **16** contrasts with the thermal stability exhibited by the side-bonded nitrile complexes **7a** and **7b**. As will be discussed later, this difference in reactivity is probably a reflection of the ability of the metal center to π-back-bond into the C≡N π^*-orbitals of the three-membered metallacycle.

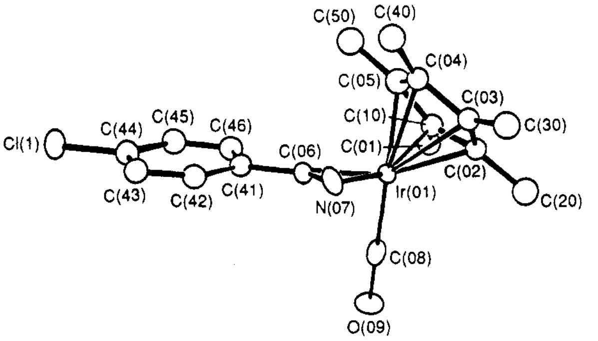


Figure 3. ORTEP projection of the side-bonded nitrile complex (η^5-C_5Me_5)(CO)Ir(η^2-NCC_6H_4) (**16**). Hydrogen atoms have been omitted for clarity.

X-ray Crystal Structure of (η^5-C_5Me_5)(CO)Ir(η^2-NCC_6H_4Cl) (16). A pentane solution of **16** was cooled to −20 °C for several days, and yellow crystals were deposited from which a suitable crystal was selected and an X-ray diffraction study was undertaken. The structure was that of the expected η^2-nitrile complex **16**. An ORTEP projection of **16** is shown in Figure 3, relevant bond distances and bond angles are given in Table I, and positional and thermal parameters are given in Table II. The iridium assumes pseudo-six-coordinate geometry with three of the coordination sites being occupied by the pentamethylcyclopentadienyl group, one by the CO, and the remaining two by the side-bonded nitrile ligand. The C–N bond distance is 1.205 Å which is comparable to the value reported for (η^5-C_5H_5)$_2$Mo(η^2-$NCCH_3$) (**8**)[24] (1.20 Å) and that which we observe for complex **7a** (1.23 Å). The N–C–C bond angle of the coordinated p-ClC_6H_4CN is 141° in complex **16** whereas in complex **7a** this angle has a value of 136°. The greater reactivity of **16** compared to **7a** and **7b** may reflect the decrease in π-back-bonding from the metal to the nitrile ligand which, in turn, may enhance the rate of ligand dissociation. In **16**, the Ir–C(6) bond length of 2.041 Å is the expected distance for an Ir–C bond[1e,25] while the Ir–N bond length of 2.185 Å represents a long Ir–N single bond.[26]

Thermolysis of (η^5-C_5Me_5)(CO)Ir(η^2-NCC_6H_4Cl) (16) in Benzene. To confirm that the side-bonded nitrile complex **16** could independently activate hydrocarbons, a sample of this material was maintained at 50 °C in C_6D_6 in the dark for 25 days. A resonance at 1.62 ppm identified the product, (η^5-C_5Me_5)Ir(CO)(D)(C_6D_5) (**17**), in 70% yield by ^{1}H NMR, demonstrating that **16** could independently activate the C–H bonds of benzene. The dimer, [(η^5-C_5Me_5)Ir(μ-CO)]$_2$ (**13**), was observed in 23% yield. On repeating the reaction under the same conditions both the rate of conversion of **16** to products and the ratio of C–H activation product **17** to dimer **13** could not be consistently reproduced even when the same bulk sample of **16** was used (Table III). The reaction appeared to randomly proceed by one of two extreme pathways. One set of reactions proceeded relatively rapidly with a half-life of about 9 days leading to **17** as the major product (about 4:1 ratio of **17**:**13**). The thermolysis of other samples of **16** proceeded more slowly ($t_{1/2} \simeq$ 26 days) and led to dimer **13** as the major product (about 1:3 ratio of **17**:**13**). To determine whether these inconsistent results were due to trace amounts of a Brønsted acid, the thermolysis of **16** in C_6D_6 was carried out in the presence of 0.05 equiv of trifluoroacetic acid. This reaction produced dimer **13** in 86.8% yield and **17** in 4% yield after 23 days. Under these conditions, the presence of acid did not promote the C–H activation product but led to the relatively rapid ($t_{1/2} \simeq$

Table III. Product Distribution Resulting from the Thermolysis of (η^5-C_5Me_5)(CO)Ir(η^2-NCC_6H_4Cl) (16) in Benzene-d_6[a]

	a				b				c	d	e	f	g	h	i
% C–H activation product 17	9.4	9.3	9.1	71.2	22.4	61.9	56.6	9.3	3.0	4.3	26.0	5.8	2.5	7.0	3.8
% dimer 13	66.0	70.9	76.0	28.8	26.9	18.0	31.6	55.6	86.8	4.3	32.0	3.5	6.2	19.7	15.4

[a] All samples were maintained at 50 °C in the dark, and compounds **17** and **13** were the only products of the thermolysis of **16**. Product distribution expressed as percent of **16** converted to **17** and **13** after stated time interval: a, Samples of **16** after 43 days; b, Samples of **16** after 37 days; c, **16** + 0.05 equiv of CF_3CO_2H after 23 days; d, **16** + 0.001 equiv of CF_3CO_2H after 21 days; e, **16** + 0.05 equiv of triethylamine after 21 days; f, **16** + 0.01 equiv of triethylamine after 21 days; g, **16** + 0.001 equiv of triethylamine after 21 days; h, **16** + 0.01 equiv of H_2O after 14 days; i, **16** + 0.01 equiv of acetic acid and 0.01 equiv of triethylamine after 14 days.

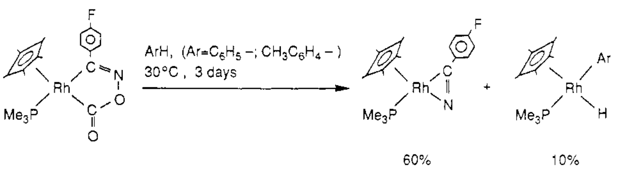
7.2 days) formation of dimer **13** in higher yield. When the thermolysis of **16** was carried out in the presence of 0.05 equiv of triethylamine to remove any spurious acid that may have been present, the reaction proceeded slowly ($t_{1/2}$ = 20 days) generating **17** in 16% yield and dimer **13** in 22% yield after 40% decomposition of the starting side-bonded nitrile complex **16**. With different concentrations of triethylamine (0.01 and 0.001 equiv), the reaction proceeded in the same manner. Carrying out the reaction in the presence of 0.01 equiv of H_2O or with a combination of 0.01 equiv of triethylamine and 0.01 equiv of acetic acid had no marked effect on the rate of reaction and the yield of **17**.

At the present time, we are unable to present a satisfactory explanation for the inconsistencies we observed in the rate and product distribution of the thermolysis of **16** in benzene. Our results suggest that under the reaction conditions the reactive metal fragment "(η^5-C_5Me_5)Ir(CO)",[2] believed to be responsible for the C–H activation products, is not directly released from **16**, as appears to occur in the photolysis of the same complex in hydrocarbon solvents discussed below. Rather the loss of the nitrile ligand to release a reactive metal species under thermolytic conditions is probably a multistep process which is subject to as yet unknown experimental factors. Further investigation of the reactivity of **16** and other side-bonded nitrile complexes reported in this paper are necessary to obtain further insights into the mechanism of this reaction.

C–H Bond Activation by Photolysis of (η^5-C_5Me_5)(CO)Ir{η^2-C(p-ClC_6H_4)NOC(=O)-} (9). The metallacycle (η^5-C_5Me_5)(CO)Ir{η^2-C(p-ClC_6H_4)NOC(=O)-} (**9**) was readily decomposed by mild photolysis using a 100-W light bulb as a light source. When a sample of **9** was maintained in benzene at 50 °C and photolyzed for 36 h, the phenyl hydride complex **11** was observed in 75.4% yield by NMR. The dimer **13**[29] was observed to be produced in 7.5% yield. When the reaction was carried out in C_6D_6 and the ^1H NMR spectrum of the reaction products taken after 12 h, resonances corresponding to the side-bonded nitrile complex **16** were observed, although only at low concentrations, suggesting that **16** was an intermediate in the photolytic decomposition of **9** although it was rapidly converted to the phenyl hydride product under these conditions. When the photolysis of **9** was carried out in cyclohexane, a solvent in which **9** is essentially insoluble, the cyclohexyl hydride complex **14**[2a] was observed after 13 days at 50 °C. Addition of CCl_4 converted **14**[2a] to the chloride derivative **15**[2a] in 48.7% overall yield by NMR analysis while compound **13** was obtained in 33.7% yield. The apparent slowness of this reaction is probably a result of the low solubility of **9** in cyclohexane.

C–H Bond Activation by Photolysis of (η^5-C_5Me_5)(CO)Ir(η^2-NCC_6H_4Cl) (16). When a sample of **16** was irradiated in benzene under the conditions described above for 12 h, it was converted in 80.6% yield to the phenylhydrido iridium complex **11**. Compound **13**[29] was estimated to have been produced in 4.7% yield by NMR. The side-bonded nitrile complex **16** thus appeared to be particularly labile under photolytic conditions, rapidly losing its nitrile ligand to presumably generate the reactive metal fragment "(η^5-C_5Me_5)Ir(CO)"[2] which leads to the observed products. When the soluble side-bonded nitrile complex **16** was photolyzed in cyclohexane, C–H activation of the solvent occurred after 24 h generating **14**.[2a] Addition of CCl_4 produced the cyclohexyl chloride **15** in 67.1% overall yield; the dimer **13**[29] was observed in 13.1% yield. The photosensitivity of **16** under these mild conditions and its high solubility in hydrocarbon solvents made it an excellent precursor complex for C–H activation.[2] Unlike the thermal reactions of **16** in benzene, photolysis of the same complex in both benzene and cyclohexane rapidly results in C–H bond activation of the hydrocarbon solvents which strongly contrasts with the slow and inconsistent reaction rates we observe in the thermolysis of **16** in benzene. Different mechanisms are obviously operative in the thermal and photochemical reactions of **16** in hydrocarbon solvents. Synthesis of the side-bonded nitrile complex **16** from the metallacycle **9** followed by mild photolysis of **16** in hydrocarbon solvents provides a high yield route for the synthesis of iridium alkyl and aryl hydrides.

Scheme XI



Thermolysis of (η^5-C_5Me_5)(PMe_3)Rh{η^2-C(p-FC_6H_4)NOC(=O)-} (10). When a toluene solution of the metallacycle **10** was maintained at 30 °C in the dark for 3 days, C–H bond activation of the meta and para positions of toluene was observed to generate (η^5-C_5Me_5)(PMe_3)Rh(m-$C_6H_4CH_3$)(H) and (η^5-C_5Me_5)(PMe_3)Rh(p-$C_6H_4CH_3$)(H) in 4% and 2% yields, respectively. This statistical ratio is quite similar to the isomer distribution reported by Jones et al. in the photolysis of (η^5-C_5Me_5)Rh$(H)_2$(PMe_3).[4] When **10** was maintained in C_6H_6 for 3 days in the dark at 30 °C, the phenyl hydride complex (η^5-C_5Me_5)(PMe_3)Rh(C_6H_5)(H)[4] was obtained in 10% yield (Scheme XI). In addition to the hydride resonances due to C–H bond activation of the solvent, when **10** was decomposed in either benzene or toluene, two additional sets of doublets of doublets were observed in the hydride region of the ^1H NMR spectrum centered at −12.26 ppm (J = 29.7, 46.3 Hz) and −13.54 ppm (J = 30.2, 48.1 Hz). These resonances, while not specifically assigned, were attributed to the products of presumably intramolecular C–H bond activation of the 2- and 3-positions of 1-fluoro-4-cyanobenzene in a combined yield of about 3%. The major product of the thermolysis of **10** in either benzene or toluene was the side-bonded nitrile complex (η^5-C_5Me_5)(PMe_3)Rh(η^2-NCC_6H_4F) (**18**), observed in 60% yield by NMR when **10** was decomposed in toluene. This product was isolated by removal of the solvent from the thermolysis reactions of **10** and extraction with pentane. The resulting red solution was cooled to −30 °C, affording red crystals of **18** characterized by IR and ^{1}H NMR spectroscopy and elemental analyses. Compound **18** decomposed when handled in air, and crystals turned opaque on removal from the solution, preventing an X-ray diffraction study from being undertaken. In common with the other side-bonded nitrile complexes discussed in this paper (**7a**, **7b**, and **16**) **18** showed a characteristic absorption at 1794 cm^{-1} attributed to the CN bond stretch. Unlike the iridium nitrile complex **16**, $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(\eta^2\text{-}NCC_6H_4F)$ was demonstrated to not be an intermediate in the activation of the benzene or toluene solvent by **10**. When a sample of **18** was maintained at 30 °C in the dark in toluene for 3 days, no C–H activation products were observed. This result might be rationalized by the presumption that the trimethylphosphine ligand renders the rhodium center electron-rich, and, as a result, the nitrile ligand is not as readily displaced as it was in **16**. The enhanced stability of the nitrile complex on substitution of a phosphine ligand at the metal center must also account for the thermal stability of **7a** and **7b**. The fact that **18** did not independently insert into the C–H bonds of toluene under thermolytic conditions suggests that the metal fragment "$(\eta^5\text{-}C_5Me_5)Rh(PMe_3)$",[1f,3,4] believed to be responsible for the C–H activation reactions, was released directly by the metallacycle **10** or that another mechanism prevails. This contrasts with the iridium system where the reactive intermediate "$(\eta^5\text{-}C_5Me_5)Ir(CO)$"[2] or a functionally equivalent species appeared to be released by the intermediate nitrile complex **16** during thermolysis. The nitrile complexes **7a**, **7b**, **16** and **18**, like the metallacycles from which they are derived, demonstrate a wide range of stabilities which closely parallel those of their parent metallacycles since in both cases kinetic stabilities are proportional to the electron density present at the metal center.

Conclusions

The present work demonstrates a new set of mild thermal and photochemical pathways for C–H bond activation that make use of novel side-bonded aryl nitrile complexes derived from the corresponding $(\eta^5\text{-}C_5Me_5)(CO)Ir\{\eta^2\text{-}C(Ar)NOC({=}O)\text{-}\}$ metallacycles. While the photochemical decomposition of side-bonded nitrile complexes, such as **16**, quite likely proceeds to generate the reactive C–H activation intermediate "$(\eta^5\text{-}C_5Me_5)Ir(CO)$", this intermediate is probably not the species responsible for thermolytic C–H bond activation since the latter process is quite slow and subject to kinetic vagaries. These characteristics suggest a more complex set of mechanisms for the thermally driven and competitive reactions leading to C–H bond activation and dimer **13** from **16**. More work in the mechanistic area is clearly required with both the iridium- and rhodium-centered systems described here in order to better define the scope and utility of these C–H activation processes and the reactivity of the new side-bonded nitrile complexes, themselves. Such an effort is in progress.

Experimental Section

General Procedures. 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 and toluene were distilled from potassium metal; pentane was first stirred for 48 h over concentrated sulfuric acid and then distilled over calcium hydride, before final distillation from a solution of sodium benzophenone ketyl. Methylene chloride, carbon tetrachloride and acetonitrile were distilled from P_2O_5, and methanol was distilled from magnesium methoxide. The metal carbonyl complexes $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$,[30] $(\eta^5\text{-}C_5Me_5)Rh(CO)_2$,[31] $(\eta^5\text{-}C_5Me_5)Rh(CO)(PMe_3)$,[31] and $(\eta^5\text{-}C_5Me_5)Ir(CO)(PMe_3)$[32] were prepared according to literature procedures as was pentamethylcyclopentadiene.[33] The metallacycles **1a**, **1b**, **9**, and **10** were prepared by procedures reported elsewhere.[16b] The compounds *p*-fluorobenzaldehyde, *p*-chlorobenzaldehyde, and 2,4,6-trimethylbenzaldehyde were all commercially available and were used as received to prepare the respective oximes. The method of preparation of hydroxamic acid chlorides from the respective oximes has already been reported.[16b] Trimethylphosphine and triphenylphosphine were purchased from Strem Chemical Co. and used as received. Trifluoroacetic acid and glacial acetic acid were used as received from Aldrich Chemical Co. and degassed before use; triethylamine was purchased from MCB Manufacturing Chemists, Inc., dried over molecular sieves, and degassed before use. Elemental analyses for compounds **7a**, **7b**, **16**, and **18** were carried out by Galbraith Laboratories, Inc., Knoxville, TN. IR spectra for all these compounds were recorded on a Beckman FT-1100 instrument. ^{1}H NMR, $^{31}P\{^1H\}$ NMR, and ^{19}F NMR spectra for compounds **7a** and **7b** were recorded on a JEOL FX-90 (89.55 MHz) instrument. All other ^{1}H NMR spectra were recorded on a Bruker WM-500 spectrometer (500.13 MHz). The ^{31}P chemical shifts were referenced to external 85% H_3PO_4; ^{1}H NMR were referenced either to residual ^{1}H resonances in deuteriated solvents or to internal tetramethylsilane. The ^{19}F chemical shifts were referenced to external hexafluorobenzene (δ 0.00). Deuteriated solvents were purchased from Cambridge Isotopes. Methylene-d_2 chloride was dried over P_2O_5; benzene-d_6 and toluene-d_8 were dried over sodium benzophenone ketyl.

NMR Tube Reactions. All the solvents used for these reactions were dried and degassed before use and then vacuum transferred into NMR tubes. In a typical reaction, about 0.8 mL of solvent was added to 8.0 mg of metallacycle and maintained at a constant temperature. When the reaction was complete, the solvent was removed under vacuum and benzene-d_6 was added and the spectrum recorded. Yields were measured relative to an added quantitative amount of hexamethyldisiloxane as an internal standard or by measuring the relative integrated intensities of the product resonances relative to one another. Due to the photosensitivity of the compounds discussed, precautions were taken to ensure that all thermal reactions were carried out in the absence of any direct or indirect source of light. Photochemical experiments were carried out by using a 100-W tungsten bulb which was supported 6 in. above a constant temperature oil bath. The bulb and oil bath were wrapped in aluminum foil to contain the light radiated and also exclude any other source of light. A stream of cold nitrogen gas was used to cool the system to the desired temperature. The rhodium aryl hydrides $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(p\text{-}C_6H_4CH_3)(H)$, $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(m\text{-}C_6H_4CH_3)(H)$, and $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(C_6H_5)(H)$, were identified by matching the ^{1}H NMR chemical shifts with reported values.[4] The iridium phenyl hydride complex **11** and the iridium cyclohexylhydride product **14** were identified in a similar manner[2a] or converted to the corresponding chlorides **12**[2a,28] and **15**[2a] by addition of CCl_4. The dimer $[(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}CO)]_2$ (**13**) was identified by its ^{1}H NMR resonance at 1.58 ppm in C_6D_6.[29] Due to the duration of these reactions, they could be conveniently followed by using ^{1}H NMR spectroscopy by running the reaction in deuteriated solvents and observing the pentamethylcyclopentadienyl region of the spectrum.

Crystallographic Measurements. Collection and Reduction of X-ray Data for $(\eta^5\text{-}C_5H_5)(PPh_3)Ir(\eta^2\text{-}NCC_6H_4Cl)$ (7a). A yellow-brown parallelepiped crystal of **7a** was selected having the orthorhombic space group *Pcan* (standard setting *Pbcn*) with a = 10.628 (2) Å, b = 14.298 (3) Å, c = 33.310 (5) Å, V = 5066 Å^3, and Z = 8. Data were collected on a locally constructed diffractometer (built by Professor C. E. Strouse of this department). Intensity data were collected by using the θ–2θ scan technique. Further details about the data collection are given in Table I. Reflections were corrected for Lorentz and polarization

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effects by means of the CARESS program.[34] All calculations were performed on a VAX 11/750 computer of the J. D. McCullough X-Ray Crystallography Laboratory. Scattering factors for all non-hydrogen atoms were taken from ref 35 while those for hydrogen were from Stewart et al.[36] Anomalous dispersion terms $\Delta f'$ and $\Delta f''$ were included for Ir and P. Data were collected at 25 °C. Systematic absences were found for reflections $hk0$, $h + k = 2n + 1$, $h0l$, $h = 2n + 1$, and $0kl$, $l = 2n + 1$, an unambiguous determination of the orthorhombic space group.

Solution and Refinement of the Structure of (η^5-C_5H_5)(PPh_3)Ir(η^2-NCC_6H_4Cl) (7a). The heavy-atom method was used to locate all non-hydrogen atoms. Hydrogen atoms were placed in located positions and included in structure factor calculations with U values based on those of the attached atom, but their parameters were not refined. In the final least-squares cycle, 307 parameters were refined, including positional and anisotropic thermal parameters for one Ir, thirty C, one Cl, one N, and one P. Refinement converged at $R = 0.077$, $R_w = 0.086$, and GOF = 2.26.

Collection and Reduction of X-ray Data for (η^5-C_5Me_5)(CO)Ir(η^2-NCC_6H_4Cl) (16). A golden-brown parallelepiped of **16** was mounted on a locally modified Picker FACS-1 diffractometer equipped with a graphite monochromator, Mo Kα radiation. The compound crystallized in the monoclinic space group $P2_1/a$ with (at 298 K) $a = 7.859$ (2) Å, $b = 20.010$ (4) Å, $c = 11.721$ (2) Å, $\beta = 108.757$ (4)°, $V = 1745$ Å^3, and $\rho_{(calcd)} = 1.88$ g cm^{-3}. Data were collected by using the θ–2θ scan technique. Further details about the data collection are given in Table IV. Treatment of these measurements was similar to that for **7a**. Systematic absences were found for $0k0$, $k = 2n + 1$, and for $h0l$, $h = 2n + 1$.

Solution and Refinement of the Structure of (η^5-C_5Me_5)(CO)Ir(η^2-NCC_6H_4Cl) (16). The heavy-atom method was used to locate all non-hydrogen atoms. Hydrogen atoms were located on difference electron density maps. Hydrogen atoms of methyl groups were then placed in calculated positions with C–H = 1.0 Å and H–C–H = 109.5°. Other hydrogen atoms were included in located positions in structure factor calculations, but their parameters were not varied. Thermal parameters for hydrogen of methyl groups were fixed at $U = 0.05$ Å^2, and for all other H, $U = 0.04$ Å^2. Positional and anisotropic thermal parameters were refined for all non-hydrogen atoms with the exception of C(40), a methyl carbon atom. Least-squares refinement of 209 parameters converged at $R = 0.0385$, $R_w = 0.0582$, and GOF = 2.36.

Thermolysis of (η^5-C_5Me_5)(CO)Ir{η^2-C(*p*-ClC_6H_4)NOC(=O)–} (9) in Benzene. A sample of **9** (8.4 mg, 0.016 mmol) was placed in an NMR tube to which 0.8 mL of benzene was vacuum transferred and the sample was maintained at 50 °C for 5 weeks in the dark. The metallacycle completely dissolves after about 4 days, and the color of the solution turns from pale yellow to a darker yellow as the reaction progresses. After the reaction was complete, the benzene was removed under vacuum and benzene-d_6 was vacuum transferred to the tube which was then sealed. The ^{1}H NMR was recorded: ^{1}H NMR (C_6D_6) δ 7.68–7.66 (m, C_6H_5, *o*-H), 7.10–7.08 (m, C_6H_5, *m*- and *p*-H), 1.62 (s, C_5Me_5), −15.07 (s, IrH). These resonances were assigned to the phenylhydrido complex (η^5-C_5Me_5)Ir(CO)(H)(C_6H_5) (**11**) obtained in 90.4% yield by NMR spectroscopy. To convert **11** to the chloride derivative **12** after removal of the benzene solvent, when the reaction was complete, about 0.8 mL of CCl_4 was vacuum transferred into the NMR tube and allowed to react with **11** for several hours at room temperature. The CCl_4 was then removed under vacuum, and benzene-d_6 was vacuum transferred in and the ^{1}H NMR spectrum identified (η^5-C_5Me_5)Ir(CO)(C_6H_5)(Cl)[2a] (**12**) in 90% yield.

Thermolysis of (η^5-C_5Me_5)(CO)Ir{η^2-C(*p*-ClC_6H_4)NOC(=O)–} (9) in Cyclohexane. Cyclohexane (0.8 mL) was vacuum transferred into an NMR tube containing compound **9** (8.4 mg, 0.016 mmol). The solution was maintained at 50 °C in the dark for 5 weeks. When the reaction was complete, the cyclohexane was removed under vacuum and CCl_4 was added converting the cyclohexyl hydride **14**[2a] to the chloride derivative **15**.[2a] The CCl_4 was then removed under vacuum and C_6D_6 added. The known cyclohexyl chloride **15**[2a] was identified by ^{1}H NMR spectroscopy in 3% yield, and the dimer **13**[29] was observed in 65% yield.

Thermolysis of (η^5-C_5Me_5)(CO)Ir(η^2-NCC_6H_4Cl) (16) in Benzene-*d*$_6$. Benzene-d_6 (0.8 mL) was vacuum transferred into a sample of (η^5-C_5Me_5)Ir(CO)(η^2-NCC_6H_4Cl) (**16**) (7.3 mg, 0.015 mmol) and the tube sealed. The sample was maintained at 50 °C in the dark for 5 weeks. The products (η^5-C_5Me_5)Ir(CO)(D)(C_6D_5) (**17**) and **13** were identified by ^{1}H NMR spectroscopy. As reported in the Discussion the rate of this reaction and the ratio of the products **17** and **13** varied. On other occasions and under the same apparent conditions, the reaction appeared to proceed with a half-life of 9 days yielding **17**:**13** in a ratio of 4:1 or with a half-life of 26 days yielding **17**:**13** in the ratio of 1:3.

Thermolysis of (η^5-C_5Me_5)Ir(CO)(η^2-NCC_6H_4Cl) (16) in Benzene-*d*$_6$ in the Presence of Trifluoroacetic Acid. To a solution of **16** (10.5 mg, 0.02 mmol) in 0.6 mL of benzene-d_6 was added 0.6 μL (0.04 equiv) of a 1.3 mM solution of trifluoroacetic acid in benzene. The tube was sealed and maintained at 50 °C in the dark. After 23 days the reaction had gone to 96% completion yielding **13** in 86.6% yield and **17** in 3.3% yield based on reacted **16**.

Thermolysis of (η^5-C_5Me_5)Ir(CO)(η^2-NCC_6H_4Cl) (16) in Benzene-*d*$_6$ in the Presence of Triethylamine. To a solution of **16** (9.7 mg, 0.02 mmol) in 0.6 mL of benzene-d_6 in an NMR tube was added 0.5 μL (0.05 equiv) of a 2.04 mM solution of triethylamine in benzene. The tube was sealed and maintained at 50 °C in the dark. After 20 days and 40% conversion of **16**, compound **17** was observed in 16% yield and dimer **13** was observed in 22% yield.

Thermolysis of (η^5-C_5Me_5)Ir(CO)(η^2-NCC_6H_4Cl) (16) in Benzene-*d*$_6$ in the Presence of Acetic Acid and Triethylamine. To a solution of **16** (5 mg, 0.01 mmol) in 0.6 mmol of benzene-d_6 were added 4 μL (0.01 equiv) of a 0.025 M solution of glacial acetic acid in benzene and 42 μL (0.01 equiv) of a 2.4 mM solution of triethylamine in benzene. The reaction was maintained at 50 °C in the dark. After 8 days the reaction had gone to 13% completion yielding 11% of **13** and 2% of **17**.

Thermolysis of (η^5-C_5Me_5)Ir(CO)(η^2-NCC_6H_4Cl) (16) in Benzene-*d*$_6$ in the Presence of Water. To a solution of **16** (5 mg, 0.01 mmol) in 0.6 mmol of benzene-d_6 was added 10 μL (0.02 equiv) of a 0.025 M solution of degassed water in benzene. The reactants were maintained at 50 °C in the dark, and after 8 days the reaction had gone to 13.2% conversion of **16**, producing compound **13** in 9.6% yield and **17** in 3.6% yield.

Photolysis of (η^5-C_5Me_5)(CO)Ir{η^2-C(*p*-ClC_6H_4)NOC(=O)–} (9) in Benzene-*d*$_6$. Benzene-d_6 (0.8 mL) was vacuum transferred into an NMR tube containing 8.0 mg (0.015 mmol) of **9**. The sample was maintained at 50 °C and photolyzed (using the light source described above) for 14 h. The product (η^5-C_5Me_5)Ir(CO)(D)(C_6D_5) was identified by NMR spectroscopy in 75.4% yield. The compound [(η^5-C_5Me_5)Ir(μ-CO)]$_2$ (**13**) was also obtained in 7.5% yield.

Photolysis of (η^5-C_5Me_5)(CO)Ir{η^2-C(*p*-ClC_6H_4)NOC(=O)–} (9) in Cyclohexane. Cyclohexane (0.6 mL) was vacuum transferred into an NMR tube containing **9** (8.3 mg, 0.015 mmol). The sample was maintained at 50 °C and photolyzed for 13 days; the metallacycle enters into solution after about 8 days. The cyclohexane was then removed under vacuum, and the cyclohexylhydride product **14** was converted to the chloride derivative **15** by vacuum transfer of CCl_4. The yield of **15** based on **9** was 48.6% by NMR spectroscopy. The dimer **13** was obtained in 33.7% yield.

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[34] Functions and programs employed are given as follows: data reduction, CARESS, programs written by R. W. Broach (University of Wisconsin) and P. Coppens, P. Becker, and R. H. Blessing (SUNY Buffalo) and locally modified; Patterson and Fourier programs adapted from algorithms in MULTAN, P. Main (University of York, York, England); full-matrix least-squares and error analysis, ORFLS and ORFFE, W. R. Busing, K. O. Martin, and H. A. Levy (Oak Ridge National Laboratory) and locally modified; absorption correction, ABSN, P. Coppens; plotting program, ORTEP II, C. K. Johnson (Oak Ridge National Laboratory); SHELX 76, crystallographic package, G. Sheldrick.

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Table IV. Details of Crystallographic Data Collection

	7a	**16**
temp/K	298	128
cryst size/mm	0.45 × 0.39 × 0.39	0.27 × 0.3 × 0.43
normal to faces	001, $\bar{1}10$, 110	011, $0\bar{1}1$, $\bar{2}11$
appearance	yellow-brown parallelepiped	golden brown parallelepiped
radiatn (graphite monochromator)	Mo Kα	MoKα
wavelength/Å	0.7107	0.7107
space group	*Pcan* (standard setting *Pbcn*)	$P2_1/a$
a/Å	10.638 (2)	7.859 (2)
b/Å	14.298 (3)	20.010 (4)
c/Å	33.310 (5)	11.721 (2)
β/deg		108.757 (4)
V/Å^3	5066	1745
Z	8	4
ρ(calcd)/g cm^{-3}	1.72	1.88
μ/cm^{-1}	54.4	78.0
range of transmissn factors (av)	0.4850–0.3417 (0.4232)	0.5112–0.3053 (0.4160)
scan width		
below Kα_1	1.25	1.3
above Kα_2	1.25	1.6
scan rate/deg min^{-1}	4.5	12.0
no. of unique reflctns	4254	3065
no. of obsd ($I > 3\sigma(I)$) reflctns	2495	2709
2θ max/deg	54	50
data collected	$+h,+k,+l$	$+h,+k,\pm l$
no. of parameters refined	307	209
R,R_w, GOF	0.077, 0.086, 2.26	0.0385, 0.0582, 2.36

Photolysis of (η^5-C_5Me_5)(CO)Ir(η^2-NCC_6H_4Cl) (16) in Benzene-d_6. A sample of **16** (7.3 mg, 0.015 mmol) in 0.7 mL of benzene-d_6 was sealed in an NMR tube and maintained at 50 °C. The sample was photolyzed for 14 h and the ^{1}H NMR spectrum recorded. The product (η^5-C_5Me_5)Ir(CO)(C_6D_5)(D) was obtained in 80.6% yield and [(η^5-C_5Me_5)Ir(μ-CO)]$_2$ (**13**) in 4.7% yield.

Photolysis of (η^5-C_5Me_5)(CO)Ir(η^2-NCC_6H_4Cl) (16) in Cyclohexane. Cyclohexane (0.6 mL) was vacuum transferred into 8.3 mg (0.017 mmol) of **16** in an NMR tube. The sample was maintained at 50 °C and photolyzed for 24 h. The cyclohexane was removed under vacuum, and 0.8 mL of CCl_4 was added and the reactants were maintained at room temperature for 2 h. The CCl_4 was then removed under vacuum and benzene-d_6 added. The tube was sealed and the ^{1}H NMR spectrum obtained. (η^5-C_5Me_5)Ir(CO)(C_6H_{11})(Cl) (**15**) was identified in 67.1% yield by NMR spectroscopy, and dimer **13** was obtained in 31.1% yield.

Thermolysis of (η^5-C_5Me_5)(PMe_3)Rh{η^2-C(p-FC_6H_4)NOC(=O)-} (10) in Toluene. Toluene (0.8 mL) was vacuum transferred into an NMR sample of **10** (8.3 mg, 0.02 mmol) and maintained at 30 °C for 72 h in the dark. The toluene was removed under vacuum, and benzene-d_6 was vacuum transferred in. The ^{1}H NMR spectrum of the products was recorded, identifying (η^5-C_5Me_5)(PMe_3)Rh(m-$C_6H_4CH_3$)(H) and (η^5-C_5Me_5)(PMe_3)Rh(p-$C_6H_4CH_3$)(H) in 4 and 2% yields, respectively, and compound **18** in 60% yield.

Thermolysis of (η^5-C_5Me_5)(PMe_3)Rh{η^2-C(p-FC_6H_4)NOC(=O)-} (10) in Benzene. Benzene (0.8 mL) was vacuum transferred into an NMR sample of **10** (8.0 mg, 0.02 mmol). The tube was maintained in the dark at 30 °C for 72 h, and the benzene was removed under vacuum and benzene-d_6 was vacuum transferred in. The ^{1}H NMR of the products identified the compound (η^5-C_5Me_5)(PMe_3)Rh(C_6H_5)(H) in 13% yield and compound **18** in 80% yield.

Thermolysis of (C_5H_5)(PPh_3)Ir{η^2-C(p-FC_6H_4)NOC(=O)-} (1b) in the Presence of p-ClC_6H_4CN. Toluene-d_8 (0.6 mL) was vacuum transferred into an NMR tube containing metallacycle **1b** (20.0 mg, 0.029 mmol) and a 20-fold excess of p-ClC_6H_4CN (79.0 mg, 0.58 mmol). The tube was sealed and maintained at 110 °C for 24 h and the side-bonded nitrile (η^5-C_5H_5)(PPh_3)Ir(η^2-NCC_6H_4F) (**7b**) was identified by its ^{31}P and ^{19}F NMR resonances. No ^{31}P NMR resonances were observed corresponding to **7a**.

Synthesis of (η^5-C_5H_5)Ir(PPh_3)(η^2-NCC_6H_4Cl) (7a). Toluene (20 mL) was syringed into 0.30 g (0.50 mmol) of **1a**. The suspension was refluxed for 48 h; the metallacycle dissolved as the reaction progressed and the color turned to yellow. The toluene was removed under vacuo and the yellow residue dissolved in ether and filtered. On cooling to −30 °C, yellow crystals of **7a** were obtained in 55% yield (0.18 g, 0.28 mmol). 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. IR (Nujol): 2980–2840 (vs), 1758 (m), 1676 (w), 1608 (w), 1584 (w), 1567 (w), 1307 (w), 1191 (m), 1160 (m), 1092 (s), 1027 (w), 1013 (m), 1000 (w), 900 (w), 845 (s), 823 (s), 747 (s), 697 (vs) cm^{-1}. ^{1}H NMR (C_6D_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_6D_6): δ 16.56.

Synthesis of (η^5-C_5H_5)Ir(PPh_3)(η^2-NCC_6H_4F) (7b). The metallacycle **1b** (0.21 g) was refluxed in 20 mL of toluene for 48 h. The reactant entered into solution as the reaction progressed, and the color of the solution changed from pale yellow to orange. On completion of the reaction the toluene was removed under vacuo and the residue redissolved in ether. On cooling to −30 °C, yellow-brown crystals of **7b** were obtained in 51% yield (0.10 g). 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. IR (Nujol): 3000–2840 (vs), 1756 (s), 1590 (s), 1494 (s), 1402 (m), 1309 (w), 1004 (m), 986 (w), 890 (w), 860 (w), 837 (s), 804 (s), 787 (m), 752 (m), 748 (m), 699 (s), 639 (w), 616 (w) cm^{-1}. ^{1}H NMR (CD_2Cl): δ 7.67–6.82 (complex multiplets, 19 H), 5.27 (d, 5 H, J = 1.2 Hz). ^{31}P{^{1}H} NMR (C_6D_5–CD_3): δ 16.29. ^{19}F NMR ($C_6D_5CD_3$): δ 53.75.

Synthesis of (η^5-C_5Me_5)Ir(CO)(η^2-NCC_6H_4Cl) (16). To 0.5 g (0.9 mmol) of metallacycle **9** in a Schlenk flask was added by syringe 60 mL of THF. The reactants were freeze–pump–thawed to ensure that no oxygen was present. The Schlenk flask was wrapped in aluminum foil due to the photosensitivity of **9** and the side-bonded nitrile product **16**. The solution was maintained at 50 °C for 14 h, and during this time the solution turned orange-yellow. The THF was then removed under vacuum and the residue extracted with pentane. The pentane solution was filtered and cooled to −30 °C; yellow crystals of **16** were obtained in 66% yield (0.195 g) based on reacted **9**. **9** (0.14 g) was recovered from the residue left after extracting **16** with pentane. Anal. Calcd for $C_{18}H_{19}ClIrNO$: C, 43.85; H, 3.89; Cl, 7.19; Ir, 38.98; N, 2.84. Found: C, 43.51; H, 4.00; Cl, 6.92; Ir, 38.99; N, 2.78. IR (Nujol): 3040–2800 (vs), 1947 (vs), 1782 (m), 1680 (w), 1590 (w), 1565 (w), 1262 (w), 1190 (w), 1161 (w), 1096 (m), 1086 (m), 1030 (m), 1015 (m), 832 (m), 817 (m), 699 (w) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.72 (d, 2 H, J = 8.3 Hz), 7.01 (d, 2 H, J = 8.3 Hz), 1.69 (s, 15 H).

Synthesis of (η^5-C_5Me_5)Rh(PMe_3)(η^2-NCC_6H_4F) (18). THF (30 mL) was added to 0.45 g (0.94 mmol) of **10**. The solution was freeze–pump–thaw degassed to ensure that no oxygen was present and allowed to stir at room temperature. The yellow solution became red, and after 48 h the THF was removed under vacuum; the residue was extracted with pentane, and the resulting solution was filtered. On cooling to −30 °C red crystals of **18** were obtained in 40% yield (0.16 g). Anal. Calcd for $C_{20}H_{28}FNPRh$: C, 55.17; H, 6.50; N, 3.22; P, 7.11; Rh, 23.64. Found: C, 54.89; H, 6.65; N, 3.15; P, 6.77; Rh, 24.08. IR (Nujol): 3050–2800 (vs), 1794 (s), 1650 (w), 1589 (s), 1490 (s), 1300 (w), 1280 (m), 1214 (s), 1182 (w), 1143 (s), 1090 (w), 1070 (w), 1026 (w), 1010 (w), 948 (vs), 853 (s), 770 (w), 755 (w), 724 (w), 671 (m), 639 (m) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.93–7.90 (m, 2 H), 6.81–6.78 (m, 2 H), 1.85 (d, J = 2.2 Hz, 15 H), 0.81 (dd, J = 8.87, 0.86 Hz, 9 H).

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Registry No. **1a**, 103731-57-3; **1b**, 103731-58-4; **7a**, 103731-59-5; **7b**, 103751-00-4; **9**, 106712-24-7; **10**, 112022-79-4; **11**, 81753-18-6;

12, 32609-75-9; 13, 106682-38-6; 14, 81753-16-4; 15, 81753-17-5; 16, 106682-39-7; 17, 112022-78-3; 18, 112022-80-7; $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(m\text{-}C_6H_4CH_3)(H)$, 81971-47-3; $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(p\text{-}C_6H_4CH_3)(H)$, 81971-48-4; $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(C_6H_5)(H)$, 81971-46-2; $p\text{-}ClC_6H_4CN$, 623-03-0.

Supplementary Material Available: Listings of all positional and thermal parameters and interatomic distances and angles for **7a** and **16** (9 pages); listings of structure factors for **7a** and **16** (24 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of New (η^6-Substituted indole)(η^5-cyclopentadienyl)ruthenium Complexes. Nucleophilic Displacement upon (η^6-4- or η^6-5-Chloroindole)(η^5-cyclopentadienyl)ruthenium(II) Hexafluorophosphates

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(η^5-Cyclopentadienyl)tris(acetonitrile)ruthenium(II) hexafluorophosphate undergoes smooth thermal ligand exchange reaction with a variety of indole substrates to yield new complexes in which all three acetonitrile molecules have been replaced. Complexes prepared by this method are [(η^6-indole)RuCp]PF_6, [(η^6-*N*-methylindole)RuCp]PF_6, [(η^6-5-methyl-*N*-methylindole)RuCp]PF_6, [(η^6-5-bromoindole)RuCp]PF_6, [(η^6-5-chloro-*N*-methylindole)RuCp]PF_6, [(η^6-4-chloro-*N*-methylindole)RuCp]PF_6, and [(η^6-5-chloroindole)RuCp]PF_6. Complexes [(η^6-5-chloro-*N*-methylindole)RuCp]PF_6 and [(η^6-4-chloro-*N*-methylindole)RuCp]PF_6 undergo substitution of the chlorine atom with anions generated (NaH/THF) from dimethyl malonate, diethyl malonate, mercaptoacetic acid, and benzyl alcohol. Complexes prepared in this study were [(η^6-5-(dicarbomethoxymethyl)-*N*-methylindole)RuCp]PF_6, [(η^6-4-(dicarbomethoxymethyl)-*N*-methylindole)RuCp]PF_6, [(η^6-5-(dicarbethoxymethyl)-*N*-methylindole)RuCp]PF_6, [(η^6-4-(dicarbethoxymethyl)-*N*-methylindole)RuCp]PF_6, [(η^6-5-((*S*)-(carboxymethyl)thio)-*N*-methylindole)RuCp]PF_6, [(η^6-4-((*S*)-(carboxymethyl)thio)-*N*-methylindole)RuCp]PF_6, and [(η^6-5-(phenylmethoxy)-*N*-methylindole)RuCp]PF_6. Similarly, nucleophilic substitution reaction of [(η^6-5-chloro-*N*-methylindole)RuCp]PF_6 with methanol in the presence of excess KOH (20 molar equiv) gave [(η^6-5-methoxy-*N*-methylindole)RuCp]PF_6. Complex [(η^6-5-(methylamino)-*N*-methylindole)RuCp]PF_6 was obtained from reaction of [(η^6-5-chloro-*N*-methylindole)RuCp]PF_6 with methylamine (40% aqueous solution). Synthesis of complex [(η^6-5-(dicarbomethoxymethyl)indole)RuCp]PF_6 from complex [(η^6-5-chloroindole)RuCp]PF_6 is described using the *tert*-butyldimethylsilyl N-protecting group. Structural data such as IR, ^1H NMR, ^{13}C NMR, and microanalysis are given.

Indoles substituted at the C_4, C_5, C_6, and C_7 positions make up an important class of compounds that includes ergot alkaloids,[1] calabar bean alkaloids,[2] marine indoles,[3] synthetic β-blockers,[4] and psilocin analogues.[5] These compounds have many uses. For example, they act as adrenergics,[6] cholinergics,[7] antibiotics,[8] tumor promoters,[9] and fungicides.[10] Methods for synthesizing the 4-, 5-, 6-, or 7-substituted indole systems have so far fallen into three categories.[11] The first category includes the Leimgruber–Batcho method that proceeds from an appropriately substituted *o*-nitrotoluene and then construction of the fused pyrrole.[12] Another method in this category combines the Fischer indole reaction with the Japp–Klingemann reaction. In this method, the substituents are placed at the desired position on the indole by preselection in the benzene ring.[13] Methods in the second category start with an intact pyrrole ring and build up the benzene ring. For example, the benzene ring can be built up by photooxygenation of the pyrrole,[14] by employing the Diels–Alder

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