Preparation and Dynamic Behavior of η^3-Cyclopropenyl Complexes of Cobalt, Rhodium, and Iridium. Crystal and Molecular Structure of $[\mathrm{Ir}(\eta^3\text{-}\mathrm{C_3{}^tBu_3})(\mathrm{CO})_3]$

Russell P. Hughes,[*,†] David S. Tucker,[†] and Arnold L. Rheingold[‡]

Departments of Chemistry, Burke Chemistry Laboratory, Dartmouth College, Hanover, New Hampshire 03755-3564, and University of Delaware, Newark, Delaware 19716

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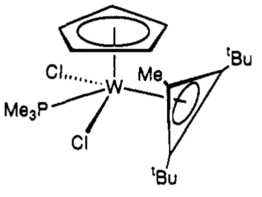
Reaction of the metal carbonyl anion [PPN]$[\mathrm{Rh(CO)_4}]$ with the cyclopropenyl cation $[\mathrm{C_3{}^tBu_3}][\mathrm{BF_4}]$ affords $[\mathrm{Rh}(\eta^3\text{-}\mathrm{C_3{}^tBu_3})(\mathrm{CO})_3]$ (**5c**), completing the group 9 triad with the previously prepared cobalt and iridium analogues **5a** and **5b**. The molecular structure of the iridium complex $[\mathrm{Ir}(\eta^3\text{-}\mathrm{C_3{}^tBu_3})(\mathrm{CO})_3]$ (**5b**) has been determined by a single crystal X-ray diffraction study: $\mathrm{C_{18}H_{27}O_3Ir}$, monoclinic, $P2_1/m$, $a = 9.422(6)$ Å, $b = 14.267(8)$ Å, $c = 14.654(12)$ Å, $\beta = 91.80(6)°$, $V = 1968.8(24)$ Å^3, $Z = 4$. Carbonyl substitution of complexes **5** readily affords the complexes $[\mathrm{M}(\eta^3\text{-}\mathrm{C_3{}^tBu_3})(\mathrm{CO})_2\mathrm{L}]$ (**10a**, M = Co, L = $\mathrm{PMe_3}$; **10b**, M = Rh, L = $\mathrm{PMe_3}$; **10c–f**, M = Ir, L = $\mathrm{PMe_3}$, $\mathrm{PPh_3}$, $\mathrm{P(OMe)_3}$, $\mathrm{CN^tBu}$). These monosubstituted complexes exhibit variable temperature ^{1}H NMR behavior with respect to cyclopropenyl rotation and the free energies of activation ($\Delta G^‡$) for $\mathrm{C_3}$ rotation about the metal–$\mathrm{C_3}$ axis have been obtained. $\Delta G^‡$ increases down the group in the order Co < Rh < Ir. Discussion of steric and electronic effects of ancillary ligands on the relative magnitudes of $\Delta G^‡$ and a comparison of these variations with those observed by others for $[\mathrm{Fe(TMM)(CO)_2L}]$ (TMM = η^4-trimethylenemethane) complexes **11** and **12** are presented.

Introduction

The dynamic behavior of transition metal–olefin complexes[1] has been the subject of extensive investigation. A large body of experimental data exists, that has been supplemented by detailed theoretical studies, and the factors responsible for the variations in the activation parameters for propeller rotation of η^2-olefins are now well understood.[2] The experimental database and theoretical understanding of rotation barriers for other organic ligands bound to transition metal centers is less comprehensive, however.[1e]



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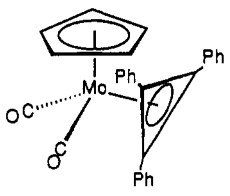

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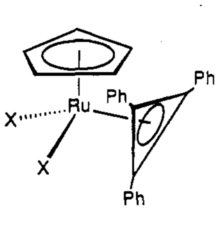
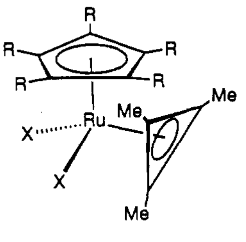


3 (X = Cl, Br, I)



4 (R = H, Me; X = Cl, Br, I)

Cyclopropenyl is the simplest cyclic organic ligand capable of metal ligation via all its ring carbon atoms, and we have been interested in the synthesis, chemistry, and dynamic behavior of η^3-cyclopropenyl complexes for some time. These compounds are valence isomeric relatives of metallacyclobutadienes, which have been implicated strongly in the mechanism of alkyne metathesis.[3] The sparse reports of their dynamic behavior with respect to rotation about the metal–$\mathrm{C_3}$ axis fell into two categories, involving either extremely fast (type 1) or extremely slow (type 2) rotation on the NMR time scale. For example, the complex **1** [a d^2 W(IV) complex; treating cyclopropenyl as a 4-electron monoanion, like allyl] contains a conformationally rigid, type 1 η^3-$\mathrm{C_3{}^tBu_2Me}$ ligand at ambient temperature,[4] but the d^4 Mo(II) complex **2** contains a fluxional, type 2 η^3-$\mathrm{C_3Ph_3}$ ligand on the NMR time scale at −80 °C.[5] While both compounds **1** and **2** contain a group 6 metal, they are so different in terms of oxidation state, cyclopropenyl substituents, and ancillary ligands on the metal that the cause of the dramatic difference in dynamic behavior is not readily apparent. Preparation of the d^4 Ru(IV) complexes **3**[6] reduced the variables to two; **2** (type 1) and **3** (type 2) are isoelectronic and possess the same triphenylcyclopropenyl ligand, although the ancillary ligands on the metal are different. Interestingly, these

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[†] Dartmouth College.

[‡] University of Delaware.

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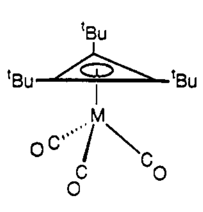
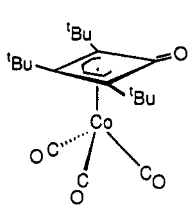
isoelectronic complexes display significantly different barriers to rotation of the cyclopropenyl ligand, with a maximum $\Delta G^{\ddagger}(2) \leq 32$ kJ mol^{-1} and a minimum $\Delta G^{\ddagger}(3) \geq 62$ kJ mol^{-1}.[6] Since crystal structures of **2**[5] and **3**[6] show that these complexes are virtually superimposable, a rationale for the difference in $\Delta G^{\ddagger}$ was sought on the basis of the electronic structure of these complexes. A detailed explanation was obtained through a theoretical analysis conducted at the extended Hückel molecular orbital (EHMO) level on model complexes [RuCp(η^3-C_3H_3)Br_2] (Cp = C_5H_5) and [MoCp(η^3-C_3H_3)$(CO)_2$].[7] More experimental information on the factors affecting $\Delta G^{\ddagger}$ was obtained in a comparison of the η^3-C_3Me_3 complexes **4**, the first series of complexes to exhibit variable temperature NMR behavior consistent with cyclopropenyl rotation.[7] Here it was noted that $\Delta G^{\ddagger}$ was virtually unaffected by changing the cyclopentadienyl ligand from C_5H_5 to C_5Me_5 and was also insensitive to changes in halogens from Cl to Br to I.

To further the understanding of the factors influencing the magnitudes of these rotational barriers in η^3-cyclopropenyl complexes, we sought a series of complexes in which the effects of changing one variable (metal or ancillary ligand) at a time could be evaluated. This presented a synthetic challenge, as some apparently attractive methods to prepare η^3-cyclopropenyl complexes lead to complexes other than those desired. One logical route might appear to be the reaction of metal carbonyl anion with a cyclopropenyl cation. This strategy has been applied to group 5,[8] 6,[9] 7,[10] 8[11] and 9[11] metal carbonyl anions but often leads to products other than η^3-cyclopropenyl compounds. Particularly common is formation of η^3-oxocyclobutenyl complexes, via CO insertion pathways which dominate the chemistry of cyclopropenyl cations with most metal carbonyl anions.[11,12]

There was evidence that this CO insertion pathway could be suppressed by using the bulky $C_3{}^tBu_3$ cation as a reagent. For example, [Ni(η^3-$C_3{}^tBu_3$)(CO)Br] has been prepared from an oxidative addition reaction of nickel carbonyl with [$C_3{}^tBu_3$][BF_4] in the presence of sodium bromide.[13] However, cyclopropenyl complexes are not the inevitable result of such reactions. Addition of tri-*tert*-butylcyclopropenyl tetrafluoroborate ([$C_3{}^tBu_3$][BF_4] to [M(η^5-C_5H_5)$(CO)_3$]$^-$ anions (M = Mo, W) affords complexes resulting from apparent electrophilic attack of the cyclopropenyl cation on the cyclopentadienyl ligand, and a similar reaction using [Fe(η^5-C_5H_5)$(CO)_3$]$^-$ affords an oxocyclobutenyl complex.[14] However, in contrast to reactions of other cyclopropenyl cations with [$Co(CO)_4$]$^-$, which invariably produce oxocyclobutenyl ligands,[12] addition of [$C_3{}^tBu_3$][BF_4] to [PPN][$Co(CO)_4$] [PPN = bis(triphenylphosphiniminium)] affords both the η^3-cyclopropenyl complex **5a** and η^3-oxocyclobutenyl complex **6**,[11] and addition of [$C_3{}^tBu_3$][BF_4] to [PPN][$Fe(CO)_3NO$] affords only the η^3-cyclopropenyl complex **7**.[11] This latter complex is isoelectronic with the hypothetical model complex [Fe(η^3-C_3H_3)$(CO)_3$]$^-$, for which the barrier to cyclopropenyl rotation has been calculated by EHMO methods to be 27.5 kJ mol^{-1}.[15]



5 a. M = Co
b. M = Ir
c. M = Rh



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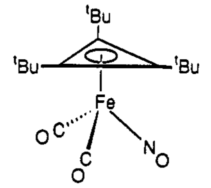

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We have described previously the synthesis of the iridium analogue **5b** via the reaction of [$Ir(CO)_4$]$^-$ with [$C_3{}^tBu_3$]$^+$; in this case no oxocyclobutenyl complex was formed.[16] Photoelectron spectroscopy (PES) studies on **5a** and **5b** show that the cyclopropenyl ligand in these complexes is best regarded as a cationic 2-electron donor and a good π-acceptor, akin to NO$^+$, and that these compounds are best described as d^{10} complexes of the metal in the −1 oxidation state.[16]

Here we report the synthesis of the rhodium relative of these compounds, the molecular structure of the iridium complex **5b**, and ligand substitution reactions of the whole triad to provide the first series of conformationally dynamic cyclopropenyl complexes in which the metal and ancillary ligands can be varied independently.

Results and Discussion

The reaction of group 9 metal carbonyl anions [$M(CO)_4$]$^-$ (M = Co, Ir) with the tri-*tert*-butylcyclopropenyl cation to prepare the cobalt and iridium complexes **5a**[11] and **5b**[16] have been described previously. The rhodium analogue **5c** was prepared in an analogous manner using the [$Rh(CO)_4$]$^-$ anion. In contrast to the cobalt system, but identical to the analogous iridium reaction, no oxocyclobutenyl ligand formation to give an analogue of **6** was observed for the rhodium reaction. As expected, each of the three compounds shows two characteristic ν_{co} bands of intensity ratio 1:2, characteristic of a C_{3v} tricarbonylmetal complex, the expected single ^{1}H NMR resonance for the *tert*-butyl groups, and four resonances in the $^{13}C\{^1H\}$ NMR spectrum. ^{103}Rh–^{13}C spin–spin coupling of 68 Hz to the carbonyl carbon and 6 Hz to the cyclopropenyl ring carbon was observed. In contrast to the Co and Ir complexes, which are white, air and thermally stable crystalline solids, the Rh analogue **5b** is a yellow, air and heat sensitive solid, making it unsuitable for PES studies

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Table I. Crystal and Refinement Data for $[Ir(\eta^3\text{-}C_3{}^tBu_3)(CO)_3]$ (5b)

		(a) Crystal Parameters	
formula	$C_{18}H_{27}O_3Ir$	V, Å^3	1968.8(24)
fw	483.63	Z	4
cryst syst	monoclinic	cryst dimens, mm	0.40 × 0.42 × 0.40
space group	$P2_1/m$	cryst color	pale yellow
a, Å	9.422(6)	D(calc), g cm^{-3}	1.63
b, Å	14.267(8)	μ(Mo Kα), cm^{-1}	71.93
c, Å	15.654(12)	temp, K	298
β, deg	91.80(6)	T(max)/T(min)	2.81
		(b) Data Collection	
diffractometer	Nicolet R3	no. of reflns collcd	3922
monochromator	graphite	no. of indpt rflns	3759
radiation	Mo Kα (λ = 0.710 73 Å)	no. of indpt obsvd rflns $F_o \geq n\sigma(F_o)$ (n = 5)	2451
2θ scan range, deg	4–52	std rflns	3/197
data collected (h,k,l)	±12, +18, +19	var in stds	<1
		(c) Refinement	
$R(F)$, %	5.82	$\Delta(\rho)$, e Å^{-3}	1.20
$R(wF)$, %	6.42	N_o/N_v	11.22
Δ/σ(max)	0.012	GOF	1.443

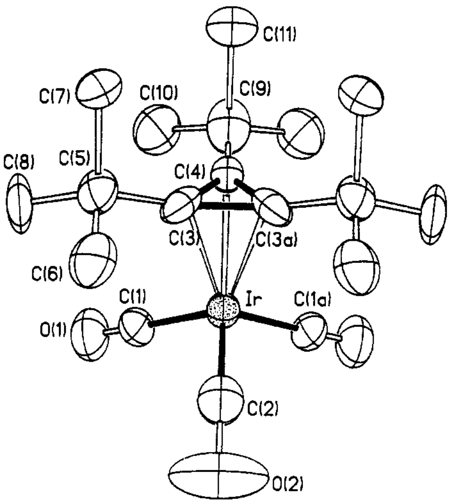

Figure 1. ORTEP representation of the molecular structure of $[Ir(\eta^3\text{-}C_3{}^tBu_3)(CO)_3]$ (**5b**).

and precluding satisfactory microanalysis results. A PMe_3 derivative has been prepared (see below) which did give good microanalysis data, and we are confident of the formulation of this compound.

The iridium complex **5b** was subjected to a single-crystal X-ray crystallographic analysis. The molecular structure and atom numbering scheme are shown as an ORTEP representation in Figure 1, crystal and refinement data are provided in Table I, and fractional atomic coordinates are given in Table II. The asymmetric unit contains two chemically similar but crystallographically independent half-molecules residing on crystallographic mirror planes. Selected bond distances and angles for both molecules are listed in Table III. Not unexpectedly, the structure reveals a symmetrical η^3-cyclopropenyl to iridium interaction within experimental error, and the ring carbon atoms are staggered relative to the carbonyl ligands, consistent with the conformation predicted by theory on the hypothetical anion $[Fe(\eta^3\text{-}C_3H_3)(CO)_3]^-$ [15] and that found experimentally for the cobalt complex $[Co(C_3Ph_3)(CO)_3]$.[17] The distance from the metal to the C_3 centroid (2.02 Å) is consistent with distances found in a variety of other cyclopropenyl complexes, which show a range of 1.92–2.07 Å.[5] As usually found for substituents bound to cyclopropenyl ligands, the *tert*-butyl substituents are bent out of the plane of the C_3 ring away from the metal. The "bend-back angle" is defined as the angle between the substituent to ring carbon bond and the vector from the ring carbon to the C_3 ring centroid. In Table IV, the bend-back angles for **5b** are compared to those of two analogues, $[Co(\eta^3\text{-}C_3Ph_3)(CO)_3]$[17] and $[WCp(\eta^3\text{-}C_3{}^tBu_2Me)(PMe_3)Cl_2]$ (**1**).[4] A comparison of **5b** to $[Co(\eta^3\text{-}C_3Ph_3)(CO)_3]$ reveals no dramatic difference in bend-back angles, but the *tert*-butyl groups in **1** are bent back considerably farther than those of **5b**, possibly due to more significant steric interactions between these substituents and the ancillary ligands on **1** compared to those in **5b**.

Table II. Fractional Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[Ir(\eta^3\text{-}C_3{}^tBu_3)(CO)_3]$ (5b)

	x	y	z	U^a
Ir	−598.0(9)	7500	5839.6(6)	52.1(3)
Ir′	2137.4(10)	7500	9417.4(6)	5.57(3)
O(1)	126(16)	9103(10)	7124(10)	104(6)
O(2)	1826(25)	7500	4477(15)	172(18)
O(1′)	3080(19)	9230(14)	8314(11)	136(9)
O(2′)	−1145(23)	7500	8988(16)	141(13)
C(1)	−129(18)	8521(12)	6634(12)	69(6)
C(2)	744(36)	7500	4954(23)	96(13)
C(3)	−2434(15)	7997(11)	5043(10)	61(5)
C(4)	−2919(22)	7500	5819(13)	46(7)
C(5)	−2647(18)	8852(13)	4461(11)	69(6)
C(6)	−1655(22)	8821(15)	3641(14)	93(8)
C(7)	−4244(17)	8843(14)	4098(13)	84(8)
C(8)	−2386(24)	9742(12)	5047(15)	104(10)
C(9)	−3733(37)	7500	6518(19)	95(13)
C(10)	−3639(24)	8368(17)	7136(15)	113(11)
C(11)	−5435(28)	7500	6097(21)	98(13)
C(1′)	2814(20)	8580(17)	8701(11)	91(9)
C(2′)	318(38)	7500	9060(17)	103(14)
C(3′)	2265(20)	7979(11)	10795(9)	65(6)
C(4′)	3589(24)	7500	10575(13)	58(8)
C(5′)	1687(21)	8822(12)	11297(12)	71(7)
C(6′)	128(25)	8864(17)	11237(17)	128(12)
C(7′)	2329(23)	8840(14)	12283(11)	94(9)
C(8′)	2330(29)	9728(13)	10841(17)	134(12)
C(9′)	5205(25)	7500	10654(15)	59(8)
C(10′)	5867(31)	8278(21)	10188(16)	165(17)
C(11′)	5690(32)	7500	11692(23)	157(22)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Precedence for carbonyl substitution in cyclopropenyl metal carbonyl complexes is found in the known complexes **8**[11] and **9**[18] which were both prepared from the corre-

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Table III. Selected Bond Distances and Angles for $[Ir(\eta^3\text{-}C_3{}^tBu_3)(CO)_3]$ (5b)

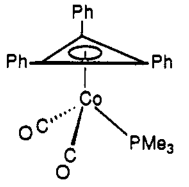
	molecule A	molecule B
(a) Bond Distances (Å)		
Ir–C(1)	1.91(2)	1.98(2)
Ir–C(2)	1.84(3)	1.78(4)
Ir–C(3)	2.18(2)	2.13(1)
Ir–C(4)	2.19(2)	2.15(2)
O(1)–C(1)	1.12(2)	1.12(3)
O(2)–C(2)	1.25(4)	1.38(4)
C93)–C(4)	1.43(2)	1.47(3)
C93)–C(3a)	1.42(3)	1.37(3)
C(3)–C(5)	1.50(2)	1.52(2)
C(4)–C(9)	1.30(4)	1.52(3)
(b) Bond Angles (deg)		
Ir–C(1)–O(1)	177.6(15)	173.5(19)
Ir–C(2)–O(2)	169.3(27)	167.3(21)
C(1)–Ir–C(2)	106.2(8)	99.7(7)
C(1)–Ir–C(3)	104.1(7)	104.0(7)
C(2)–Ir–C(3)	100.0(10)	107.7(9)
C(3)–C(4)–C(3a)	59.6(15)	55.5(15)
C(4)–C(3)–C(3a)	60.2(7)	62.2(7)

Table IV. Substituent Bend-Back Angles for Selected η^3-Cyclopropenyl Complexes

complex	bend-back angle,[a] deg
$[Ir(\eta^3\text{-}C_3{}^tBu_3)(CO)_3]$ (5b)	19.3, 19.3, 15.0
$[Co(\eta^3\text{-}C_3Ph_3)(CO)_3]$	20.3, 22.2, 15.9
$[WCp(\eta^3\text{-}C_3{}^tBu_2Me)(PMe_3)Cl_2]$ (1)	36.7 (ᵗBu), 29.5 (ᵗBu), 25.3 (Me)

[a] Values rounded to one decimal place.

sponding carbonyl derivatives by reaction with PMe_3.



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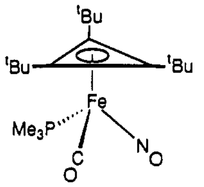

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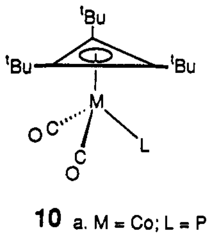
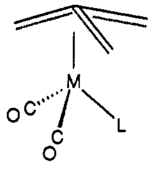
Likewise treatment of the tricarbonyl complexes 5 with a variety of tertiary phosphorus ligands led to substitution of one CO ligand and formation of complexes 10a–e. The



10 a. M = Co; L = PMe_3
b. M = Rh; L = PMe_3
c. M = Ir; L = PMe_3
d. M = Ir; L = PPh_3
e. M = Ir; L = $P(OMe)_3$
f. M = Ir; L = ᵗBuNC



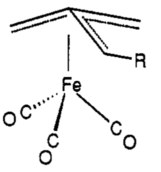
11 a. M = Fe; L = PPh_3
b. M = Os; L = PPh_3
c. M = Fe; L = ᵗBuNC

substitution reactions required significantly different degrees of thermal vigor; for the cobalt complex 5a, substitution with trimethylphosphine required 2 days in refluxing benzene, whereas the corresponding reactions of the rhodium and iridium analogues required only 3 and 4 h, respectively, at ambient temperature. A detailed study of the kinetics of these reactions shows them to be the first examples of dissociative CO substitution in the carbonyl complexes of cobalt triad.[19] Attempts to use bulky PPh_3 in substitution at the smaller cobalt center in 5a were unsuccessful, even at elevated temperatures. In addition, reaction of the iridium complex 5b with *tert*-butyl isocyanide afforded the monosubstituted complex 10f, which could be separated by sublimation from small amounts of a disubstituted analogue. The latter compound was not characterized further.

Table V. Free Energies of Activation ($\Delta G^{\ddagger}$) for Cyclopropenyl Rotation about the $M–C_3$ Axis

complex	$\Delta G^{\ddagger}$ (298 K), kJ mol⁻¹
$[Co(\eta^3\text{-}C_3{}^tBu_3)(CO)_2(PMe_3)]$ (10a)	56.7 ± 1.0
$[Rh(\eta^3\text{-}C_3{}^tBu_3)(CO)_2(PMe_3)]$ (10b)	70.9 ± 1.4
$[Ir(\eta^3\text{-}C_3{}^tBu_3)(CO)_2(PMe_3)]$ (10c)	77.2 ± 1.2
$[Ir(\eta^3\text{-}C_3{}^tBu_3)(CO)_2(PPh_3)]$ (10d)	66.1 ± 1.0
$[Ir(\eta^3\text{-}C_3{}^tBu_3)(CO)_2P(OMe_3)]$ (10e)	70.9 ± 1.3
$[Ir(\eta^3\text{-}C_3{}^tBu_3)(CO)_2(CN{}^tBu)]$ (10f)	76.7 ± 1.2
$[Fe(\eta^3\text{-}C_3{}^tBu_3)(CO)(NO)(PMe_3)]$ (9)	47.0 ± 1.0

The monosubstituted products exhibited the expected two ν_{CO} bands of equal intensity in their IR spectra. For a rigid structure, as shown for compounds 10 two *tert*-butyl resonances in a ratio of 1:2 are expected, for the ring substituent distal to ligand L and the two substituents proximal to L, respectively; if cyclopropenyl ring rotation is rapid on the NMR time scale, these resonances should coalesce to a single peak. ¹H NMR spectra taken at ambient temperature exhibited a variety of behavior; the *tert*-butyl resonances of 10a were coalesced at 22 °C, while those for 12c were decoalesced at the same temperature.



12 (R = COMe, CHOHMe, CHMeOAc, Et)

All compounds exhibited the expected variable temperature behavior of a two resonance → one resonance coalescence on going from lower to higher temperatures. The question of whether phosphorus ligand dissociation was responsible for the observed dynamic behavior was addressed by adding excess PMe_3 to an NMR tube containing 10c in toluene-d_8. Variable temperature ¹H NMR spectra showed no difference in the coalescence behavior of the cyclopropenyl ligand and the ¹H chemical shift for free PMe_3 did not coalesce with the resonance for the bound PMe_3. The variable temperature ¹H NMR spectrum of the iron analogue 9[18] was also reexamined, and decoalescence to the expected three *tert*-butyl resonances was observed at −80 °C.

These variable temperature spectra were simulated,[20] and values for the free energy of activation ($\Delta G^{\ddagger}$) for cyclopropenyl rotation about the metal-C_3 axis were calculated using the Eyring equation.[21] Values were obtained for complexes 9 and 10a–f and are compiled in Table V.

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[20] The original version of the dynamic NMR simulation program was written by: Kleier, D. A.; Binsch, G. *J. Magn. Reson.* **1970**, *3*, 146–160; Program 165, Quantum Chemistry Program Exchange, Indiana University. Modifications are described in: Bushweller, C. H.; Bhat, G.; Lentendre, L. J.; Brunelle, J. A.; Bilofsky, H. S.; Ruben, H.; Templeton, D. H.; Zalkin, A. *J. Am. Chem. Soc.* **1975**, *97*, 65–73.

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Comparison of ΔG^* values for complexes **10a–c** demonstrates that the barrier to cyclopropenyl rotation shows a significant increase on descending the group. While this general observation has been made for barriers to rotation of olefin and 1,3-diene complexes of transition metals,[2e] perhaps the best comparison is with η^4-trimethylenemethane complexes of group 8, in which the 3-fold nature of the ligand rotation is closest to that operative in compounds **10**. Based on dynamic NMR studies, the value of ΔG^* for trimethylenemethane rotation in **11a** has been shown to be 65 ± 4 kJ mol^{-},[22] whereas the corresponding osmium analogue **11b** does not show variable temperature behavior and spin-magnetization transfer experiments have shown that the lower limit to the rotation barrier must be 95 kJ mol^{-1}.[23] The effects of ancillary ligands on cyclopropenyl rotation are apparent by comparison of ΔG^* values for the series of iridium complexes **10c–f**. Clearly, ΔG^* is not directly related to steric effects of tertiary phosphorus ligands, as reflected by cone angles,[24] as the barrier for the PPh_3 complex **10d** is lower than that for the PMe_3 analogue **10c**. However there is a correlation between the basicity of the phosphorus ligand, with more strongly basic ligands affording higher values of ΔG^*. This is in direct contrast to trimethylenemethane rotation, in which more basic phosphorus ligands appear to lower the rotation barrier[22] significantly compared to those observed in their tricarbonyl analogues **12**.[25] Curiously, in our system, the more strongly accepting *tert*-BuNC ligand gives rise to a ΔG^* value for **10f** identical to that observed for the PMe_3 complex **10c**. It is noteworthy that the value of ΔG^* for trimethylenemethane rotation in the *tert*-BuNC substituted iron complex **11c** is 91 ± 6 kJ mol^{-1}, significantly higher than that for **11a** and its tertiary phosphine analogues.[22] There are clearly significant effects of electronic control in both systems that require considerable further evaluation experimentally and theoretically.

Experimental Section

General Procedures. All reactions were performed under a dinitrogen atmosphere using standard Schlenk techniques. The dinitrogen was deoxygenated over BASF catalyst and dried over Aquasorb. IR spectra were obtained on a Bio-Rad FTS 40 spectrometer. The ^{1}H (300 MHz), $^{13}C\{^1H\}$ (75 MHz), and $^{31}P\{^1H\}$ (121.4 MHz) NMR spectra were obtained on a Varian Associates XL-300 spectrometer at 22 °C unless otherwise noted. $^{31}P\{^1H\}$ chemical shifts were recorded in ppm and referenced with external 85% H_3PO_4. Chemical shifts for ^{1}H spectra and $^{13}C\{^1H\}$ spectra were recorded in ppm downfield from TMS and referenced with internal deuteriochloroform, toluene-d_8, or deuteriobenzene. Variable temperature NMR spectra were recorded on a Varian Associates XL-300 spectrometer. The probe was calibrated at various temperatures by using samples of methanol (low temperature)[26] and ethylene glycol (high temperature).[27] All solvents were dinitrogen saturated. Hydrocarbon and ethereal solvents were distilled over potassium or a sodium/potassium alloy. Methylene chloride was distilled over calcium hydride. Microanalyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI.

Starting Materials. Trimethylphosphine, triphenylphosphine, trimethyl phosphite and *tert*-butyl isocyanide were purchased from Aldrich Chemical Co. Hydrated rhodium trichloride was obtained from Johnson Matthey Aesar/Alfa. Tri-*tert*-butylcyclopropenyl tetrafluoroborate,[28] $[Co(\eta^3\text{-}C_3{}^tBu_3)(CO)_3]$,[11] $[Ir(\eta^3\text{-}C_3{}^tBu_3)(CO)_3]$,[16] and $[PPN][Rh(CO)_4]$[29] (PPN = bis(triphenylphosphiniminium) were prepared by literature procedures.

$[Rh(\eta^3\text{-}C_3{}^tBu_3)(CO)_3]$ (5c). To an orange solution of $[PPN][Rh(CO)_4]$ (1.03 g, 1.37 mmol) in THF (12 mL) was added $[C_3{}^tBu_3][BF_4]$ (0.358 g, 1.43 mmol). The white solid $[C_3{}^tBu_3][BF_4]$ dissolved slowly and the slurry turned green over the first 5 min of stirring. After more prolonged stirring the slurry then turned red/purple during the latter part of the 4-h reaction time. Volatiles were removed *in vacuo* affording an orange solid. Extraction with petroleum ether (2 × 20 mL), followed by solvent removal afforded a yellow solid which was recrystallized from hexanes to give **5c** (0.473 g, 1.20 mmol, 88%): mp 79 °C dec; IR (hexanes) ν_{CO} 2059, 2003 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.09; $^{13}C\{^1H\}$ NMR (C_6D_6): δ 193.49 (d, *C*O, $^1J_{RhC}$ = 68 Hz), 65.80 (d, $C_3{}^tBu_3$, $^1J_{RhC}$ = 6 Hz), 31.39 (CH_3), 29.53 (CMe_3). Despite repeated attempts analytically pure samples of **5c** could not be obtained.

$[Co(\eta^3\text{-}C_3{}^tBu_3)(CO)_2(PMe_3)]$ (10a). To a clear solution of $[Co(\eta^3\text{-}C_3{}^tBu_3)(CO)_3]$ (**5a**) (0.090 g, 0.026 mmol) in benzene (12 mL) was added PMe_3 (0.022 g, 0.029 mL, 0.28 mmol). The clear solution was heated to reflux and stirred for 2 days. At the end of this time a pale blue solution was observed. The volatiles were removed *in vacuo*, and the residue was filtered on a neutral alumina/petroleum ether column (3 × 1.5 cm). The resulting yellow liquid contained the product and after solvent removal afforded yellow solid **10a** which was recrystallized from hexanes (0.094 g, 0.24 mmol, 91%): mp 147 °C dec; IR (hexanes) ν_{CO} 1986, 1932 cm^{-1}; ^{1}H NMR (toluene-d_8) δ 1.22 (s br, 27 H, ^{t}Bu), 1.11 (d, 9 H, P*Me*$_3$, $^2J_{PH}$ = 6 Hz); $^{13}C\{^1H\}$ NMR (toluene-d_8, –70 °C) δ 207.9 (*C*O), 64.18 (2 C, C^tBu), 61.13 (d, 1 C, C^tBu, $^2J_{PC}$ = 12 Hz), 31.85 (6 C, CH_3), 31.45 (d, 3 C, $C(CH_3)_3$, $^4J_{PC}$ = 5 Hz), 31.44 (1 C, CMe_3), 31.01, (2 C, CMe_3), 21.81 (d, P*Me*$_3$, $^1J_{PC}$ = 21 Hz); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ –10.82. Anal. Calcd for $C_{20}H_{36}CoO_2P$: C, 60.29; H, 9.11. Found: C, 60.49; H, 9.16.

$[Rh(\eta^3\text{-}C_3{}^tBu_3)(CO)_2(PMe_3)]$ (10b). To an orange solution of $[Rh(\eta^3\text{-}C_3{}^tBu_3)(CO_3)]$ (**5c**) (0.197 g, 0.500 mmol) in hexanes (10 mL) was added PMe_3 (0.042 g, 0.050 mL, 0.550 mmol). The solution became lighter in color over the first 2 min of stirring and was allowed to stir for 3.3 h. The volatiles were removed *in vacuo*, affording orange solid **10b** (0.11 g, 0.26 mmol, 52%): mp 91 °C dec; IR (hexanes) ν_{CO} 2002, 1958 cm^{-1}; ^{1}H NMR (toluene-d_8) δ 1.28 (9 H, ^{t}Bu), 1.18 (18 H, ^{t}Bu), 1.12 (dd, 9 H, P*Me*$_3$, $^2J_{PH}$ = 6 Hz, $^3J_{RhH}$ = 1 Hz); $^{13}C\{^1H\}$ NMR (toluene-d_8) δ 196.90 (dd, *C*O, $^2J_{PC}$ = 2 Hz, $^1J_{RhC}$ = 70 Hz), 60.76 (dd, 2 C, C^tBu, $^2J_{PC}$ = 4 Hz, $^1J_{RhC}$ = 8 Hz), 57.60 (dd, 2 C, C^tBu, $^2J_{PC}$ 23 Hz, $^1J_{RhC}$ = 10 Hz), 32.29 ($C(CH_3)_3$, 6 C), 31.67 (d, 3 C, $C(CH_3)_3$, $^4J_{PC}$ = 6 Hz), 29.72 (3 C, CMe_3, two isochronous peaks), 22.64 (d, P*Me*$_3$, $^1J_{PC}$ = 17 Hz); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ –35.51 (d, $^1J_{PRh}$ = 147 Hz). Anal. Calcd for $C_{20}H_{36}O_2PRh$: C, 54.30; H, 8.20. Found: C, 54.11; H, 8.07.

$[Ir(\eta^3\text{-}C_3{}^tBu_3)(CO)_2(PMe_3)]$ (10c). To a clear solution of $[Ir(\eta^3\text{-}C_3{}^tBu_3)(CO)_3]$ (**5b**) (0.096 g, 0.198 mmol) in hexanes (10 mL) was added PMe_3 (0.017 g, 0.022 mL, 0.218 mmol). The clear solution was stirred for 4 h and did not change in appearance. The volatiles were removed *in vacuo*, affording white solid **10c** (0.61 g, 0.12 mmol, 58%). Recrystallization from hexanes afforded white cubes: mp 137 °C dec, IR (hexanes) ν_{CO} 1995, 1946 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.35 (9 H, ^{t}Bu), 1.23 (18 H, ^{t}Bu), 1.21 (d, 9 H, P*Me*$_3$, $^2J_{PH}$ = 8 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 177.65 (d, *C*O, $^2J_{PC}$ = 5 Hz), 41.35 (d, 2 C, C^tBu, $^2J_{PC}$ = 5 Hz), 37.59 (d, 1 C, C^tBu, $^2J_{PC}$ = 14 Hz), 32.72 (6 C, CH_3), 31.98 (d, 3 C, $C(CH_3)_3$, $^4J_{PC}$ = 5 Hz), 27.75 (2 C, CMe_3), 27.71 (1 C, CMe_3), 23.77 (d, $P(CH_3)_3$,

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$^4J_{PC}$ = 5 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −76.34. Anal. Calcd for $C_{20}H_{36}IrO_2P$: C, 45.18; H, 6.82. Found: C, 45.13; H, 6.75.

[Ir(η^3-$C_3{}^tBu_3$)(CO)$_2$(PPh$_3$)] (10d). A clear solution of complex **5b** (0.212 g, 0.438 mmol) in benzene (15 mL) was charged with PPh_3 (0.121 g, 0.460 mmol). The clear solution turned pale yellow while refluxing for 2 days. The volatiles were removed *in vacuo*, and the residue was filtered on a Florisil/petroleum ether column (12 × 2.5 cm). The resulting clear liquid contained the product and after solvent removal afforded white solid **10d** (0.177 g, 0.247 mmol, 56%). Recrystallization from hexanes/diethyl ether afforded white cubes: mp 174 °C dec; IR (hexanes) ν_{CO} 1998, 1950 cm^{-1}; ^1H NMR (C_6D_6) δ 7.81 (m, 6 H, Ph), 7.01 (m, 6 H, Ph), 6.92 (m, 3 H, Ph), 1.43 (br s, 9 H, ^{t}Bu), 1.07 (br s, 18 H, ^{t}Bu); $^{13}C\{^1H\}$NMR (C_6D_6) δ 178.50 (d, *C*O, $^2J_{PC}$ = 2 Hz), 138.93 (d, *ipso-C* PPh, $^1J_{PC}$ = 38 Hz), 134.10 (d, *ortho-C* PPh, $^2J_{PC}$ = 12 Hz), 129.62 (d, *para-C* PPh, $^4J_{PC}$ = 2 Hz), 128.19 (d, *meta-C* PPh, $^3J_{PC}$ = 10 Hz), 44.00 (d, 2 C, *C*^{t}Bu, $^2J_{PC}$ = 4 Hz), 38.8 (d, 1 C, *C*^{t}Bu, $^2J_{PC}$ = 22 Hz), 32.26 (6 C, *C*H$_3$), 32.06 (3 C, *C*H$_3$), 28.54 (1 C, *C*Me$_3$), 28.08 (2 C, *C*Me$_3$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −7.62. Anal. Calcd for $C_{35}H_{42}IrO_2P$: C, 58.56; H, 5.90. Found: C, 58.64; H, 5.99.

[Ir(η^3-$C_3{}^tBu_3$)(CO)$_2$P(OMe)$_3$] (10e). A clear solution of complex **5b** (0.188 g, 0.389 mmol) in hexanes (10 mL) was charged with fresh distilled P(OMe)$_3$ (0.053 g, 0.050 mL, 0.43 mmol). The clear solution stirred for 3 h, and then the volatiles were removed *in vacuo*, affording white solid **10e** (0.226 g, 0.389 mmol, 100%). Recrystallization from hexanes afforded white cubes: mp 143 °C dec; IR (hexanes) ν_{CO} 2003, 1956 cm^{-1}; ^1H NMR (C_6D_6) δ 3.28 (d, 9 H, O*Me*, $^3J_{PC}$ = 12 Hz), 1.36 (br s, 9 H, ^{t}Bu), 1.34 (br s, 18 H, ^{t}Bu); $^{13}C\{^1H\}$ NMR (toluene-d_8) δ 176.27 (d, *C*O, $^2J_{PC}$ = 5 Hz), 51.28 (d, O*Me*, $^2J_{PC}$ = 4 Hz), 43.70 (d, 2 C, *C*^{t}Bu, $^2J_{PC}$ = 4 Hz), 39.44 (d, 1 C, *C*^{t}Bu, $^2J_{PC}$ = 35 Hz), 32.38 (*C*H$_3$, 6 C), 32.03 (d, 3 C, C(*C*H$_3$)$_3$, $^4J_{PC}$ = 7 Hz), 28.31 (d, 1 C, *C*Me$_3$, $^3J_{PC}$ = 3 Hz), 27.91 (2 C, *CMe*$_3$); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ −60.75. Anal. Calcd for $C_{20}H_{36}IrO_5P$: C, 41.44; H, 6.26. Found: C, 41.56; H, 6.26.

[Ir(η^3-$C_3{}^tBu_3$)(CO)$_2$(CN^{t}Bu)] (10f). A clear solution of complex **5b** (0.183 g, 0.378 mmol) in petroleum ether (5 mL) was charged with CN^{t}Bu (0.0338 g, 37.8 μL, 0.400 mmol). The clear solution stirred for 34 h, and then the volatiles were removed *in vacuo*, affording white solid **10f** contaminated with **5b** and some [Ir(η^3-$C_3{}^tBu_3$)(CO)(CN^{t}Bu)$_2$] (IR (hexanes) ν_{CN} 2100, 2068 cm^{-1}, ν_{CO} 1946 cm^{-1}; ^1H NMR (C_6D_6) δ 1.49 (18 H, C$_3{}^t$*Bu*$_3$), 1.48 (9 H, C$_3{}^t$*Bu*$_3$), 0.95 (18 H, CN^t*Bu*)). Purification by gradient sublimation afforded **5b** (0.083 g, 0.154 mmol), 41%) as white cubes: mp 111–114 °C dec; IR (hexanes) ν_{CN} 2139 cm^{-1}, ν_{CO} 2001, 1959 cm^{-1}; ^1H NMR (C_6D_6) δ 1.33 (27 H, C$_3{}^t$Bu$_3$); 0.83 (9 H, CN^{t}Bu); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 175.01 (*C*O), 56.33 (N*C*^{t}Bu), 41.29 (2 C, C$_3$-^{t}Bu), 38.28 (1 C, C$_3$-^{t}Bu), 32.04 (6 C, C$_3$(C*Me*$_3$)$_3$), 31.57 (3 C, C$_3$(*CMe*$_3$)$_3$), 30.81 (N*C*Me$_3$), 30.53 (NC*Me*$_3$), 27.96 (2 C, C$_3$-(*C*Me$_3$)$_3$), 27.52 (1 C, C$_3$(*C*Me$_3$)$_3$). Anal. Calcd for $C_{22}H_{36}IrNO_2$: C, 49.05; H, 6.73. Found: C, 49.10; H, 6.47.

X-ray Crystallographic Determination of [Ir(η^3-$C_3{}^tBu_3$)-(CO)$_3$] (5b). A crystal suitable for X-ray structural determination was mounted on a glass fiber with epoxy cement. Crystal parameters and data collection and refinement parameters are collected in Table I. The systematic absences in the diffraction data established the space group as $P2_1/m$ or $P2_1$. The E statistics suggested the centrosymmetric alternative, and the chemically sensible results of refinement established the space group as $P2_1/m$. An empirical correction for absorption was applied (T_{max}/T_{min}) = 2.81).

The structure was solved by heavy-atom methods that located the Ir atoms. The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses. All hydrogen atoms were included as idealized isotropic contributions (d_{CH} = 0.960 Å, $U = 1.2U$ for attached C). All non-hydrogen atoms were refined with anisotropic thermal parameters. All software and the sources of the scattering factors are contained in the SHELXTL(5.1) program library (Nicolet Corp., Madison, WI).

The asymmetric unit contains two chemically similar but crystallographically independent half-molecules residing on crystallographic mirror planes.

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Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic thermal parameters, and H-atom coordinates and isotropic thermal parameters for **5b** (4 pages). Ordering information is given on any current masthead page.

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