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Reactions of Cyclopropenyl Cations with Tricarbonylnitrosylferrate(1–), Tetracarbonylcobaltate(1–), and Octacarbonyldicobalt. Synthesis and Conformational and Configurational Stabilities of η^3-Cyclopropenyl and η^3-Oxocyclobutenyl Complexes of Iron and Cobalt. Crystal and Molecular Structure of $Fe(\eta\text{-}C_3Ph_2\text{-}t\text{-}Bu)(CO)_2(NO)$

Russell P. Hughes,*[1a,2] James M. J. Lambert,[1a] David W. Whitman,[1a] John L. Hubbard,[1a]
William P. Henry,[1a] and Arnold L. Rheingold*[1b]

Departments of Chemistry, Dartmouth College, Hanover, New Hampshire 03755, and University of Delaware, Newark, Delaware 19716

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The cyclopropenyl salt $[C_3Ph_2\text{-}t\text{-}Bu][BF_4]$ reacts with $[Co_2(CO)_8]$ to give the cyclopropenylcobalt complex $[Co(\eta^3\text{-}C_3Ph_2\text{-}t\text{-}Bu)(CO)_3]$ (**10b**) and the unsymmetrically substituted oxocyclobutenyl compound $[Co(\eta^3\text{-}C_3Ph_2\text{-}t\text{-}BuCo)(CO)_3]$ (**8b**). The reaction of tri-*tert*-butylcyclopropenyl tetrafluoroborate, $[C_3\text{-}t\text{-}Bu_3][BF_4]$, with $[PPN][Co(CO)_4]$ affords both the cyclopropenyl complex $[Co(\eta^3\text{-}C_3\text{-}t\text{-}Bu_3)(CO)_3]$ (**10c**) and the oxocyclobutenyl compound $[Co(\eta^3\text{-}C_3\text{-}t\text{-}Bu_3CO)(CO)_3]$ (**8c**). Reaction of the previously reported cyclopropenyl complex $[Co(\eta^3\text{-}C_3Ph_3)(CO)_3]$ (**10a**) with tertiary phosphite or phosphine ligands does not lead to ring expansion to give the oxocyclobutenyl ligand but affords only the products of CO substitution, $[Co(\eta^3\text{-}C_3Ph_3)(CO)_2L]$ (L = P $(OPh)_3$, PPh_3, PMe_2Ph; **12a–c**). Reactions of a variety of cyclopropenyl salts, $[C_3Ph_2R][BF_4]$ (R = Ph, H, Me, *t*-Bu), with $[PPN][Fe(CO)_3(NO)]$ afford both the cyclopropenyliron complexes $[Fe(\eta^3\text{-}C_3Ph_2R)(CO)_2(NO)]$ (**15a–d**) and the oxocyclobutenyl compounds $[Fe(\eta\text{-}C_3Ph_2RCO)(CO)_2(NO)]$ (**13a–d**). Only the unsymmetrically substituted isomers of compounds **13b–d** are formed. In contrast, reaction of $[PPN][Fe(CO)_3NO]$ with $[C_3\text{-}t\text{-}Bu_3][BF_4]$ affords only the cyclopropenyl complex $[Fe(\eta^3\text{-}C_3\text{-}t\text{-}Bu_3)(CO)_2(NO)]$ (**15e**) in high yield. Variable-temperature ^{13}C NMR studies on these cyclopropenyl compounds demonstrate that rotation about the metal–C_3 ring axis is fast on the NMR time scale at −80 °C, as predicted by theory. The cyclopropenyl–iron skeleton in complex **20** is configurationally stable on the NMR time scale, with no evidence for scrambling of diastereotopic sites via a metallacyclobutadiene intermediate. The value of $^1J(C\text{–}H)$ for the cyclopropenyl carbon atom of complex **15b** is 232 Hz, consistent with approximately sp hybridization for the carbon orbital of the C–H bond. This hybridization is also consistent with that exhibited by the organic tetrahedrane **4**. The molecular structure of **15d** has been determined by a single-crystal X-ray diffraction study. It crystallizes in the orthorhombic space group *Pbca* with $a = 8.686\ (2)$ Å, $b = 15.869\ (4)$ Å, $c = 28.53\ (1)$ Å, and $Z = 8$. The structure of **15d** confirms the η^3-cyclopropenyl bonding, and bond distances are compared to those found in the organic tetrahedrane **4**.

Introduction

Reactions of cyclopropenyl cations with transition-metal complexes have afforded an impressive array of different ligand types, in which the three-membered ring can be retained intact as an η^1- or an η^3-cyclopropenyl ligand or can undergo a variety of ring-opening or ring-expansion reactions.[3] In recent papers we have discussed these reaction types, particularly in the context of selective formation of η^3-cyclopropenyl (**1**)[4] and oxocyclobutenyl (**2**)[5] complexes of the group 6 transition metals. The latter oxocyclobutenyl complexes (**2**) have been shown to be useful precursors for a variety of useful cationic and neutral η^4-cyclobutadiene complexes of the group 6 metals.[7]

The crystallographically characterized ground state of compound **1a** contrasts dramatically with the structurally defined puckered metallacyclobutadiene ground state of complex **3**;[8] they differ only in the oxidation state of the metal and the presence of CO or Cl ligands. The cause of the different ligation of the three carbon fragment in these two compounds is not understood, but the cyclopropenylmetal structure represents a valence isomer of the metallacyclobutadiene skeleton and in terms of the isolobal analogy can be thought of as a metallatetrahedrane. Notably only a single pair of purely organic tetrahedrane and cyclobutadiene valence isomers, **4**[9] and **5**,[10] has been synthesized to date. The significance of other metallacyclobutadiene complexes **6** in the metathesis of alkynes has been amply demonstrated by the work of Schrock.[11]

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(1) (a) Dartmouth College. (b) University of Delaware.

(2) Alfred P. Sloan Research Fellow, 1980–1984.

(3) For a discussion of known transition-metal cyclopropenyl complexes and their ring-opening and ring-expansion reactions, see ref 4 and 5. For a theoretical treatment of ring-opening chemistry in these complexes, see ref 6.

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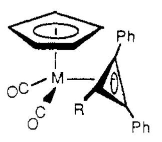
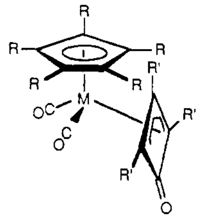
Furthermore it has been shown that metallacyclobutadiene complexes 3[8] and 6[12,13] can exhibit carbon site scrambling within the C_3 ligand on the NMR time scale and that site scrambling can also be observed in reactions of compounds 6 with alkynes to give substituted η^5-cyclopentadienyl rings; the intermediacy of the cyclopropenyl valence isomer has been proposed as a possible explanation for these phenomena.[12-15] It is apparent that definition of the subtle factors influencing the stabilities and interconvertibilities of these two organometallic valence isomers represents a challenge for both experimental and theoretical chemists.

Previously we have described detailed studies of the reactions of cyclopropenyl cations and 2-cyclopropene-1-carbonyl chlorides 7 with the tetracarbonylcobaltate(1−) anion.[16] These reactions invariably resulted in exclusive formation of (oxocyclobutenyl)cobalt complexes of general structure 8. The key precursor to ring expansion of the three-membered ring was identified as the acyl species 9, and extensive, though circumstantial, evidence against cyclopropenylcobalt intermediates was accumulated. Curiously, other workers reported that the reaction of the triphenylcyclopropenyl cation with octacarbonyldicobalt resulted in formation of the crystallographically characterized (η^3-cyclopropenyl)cobalt complex **10a** in addition to the oxocyclobutenyl analogue **8a**.[17] The mechanism of this reaction is not understood.

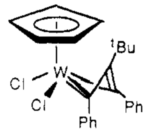
In order to establish conclusively whether cyclopropenylmetal species can be important intermediates in the ring-expansion to give oxocyclobutenyl ligands, we have extended our studies to include reactions of the isoelectronic tricarbonylnitrosylferrate(1−) anion and have also investigated some other cobalt chemistry. This paper describes the synthesis and characterization of new η^3-cyclopropenyl complexes of cobalt and iron, together with some oxocyclobutenyl relatives, and a study of the configurational stability of the cyclopropenyl–Fe and –Co framework vis-â-vis valence isomerization to a metallacyclobutadiene. The following paper presents the results of a detailed study of the exogenous ligand-induced ring-expansion reactions of cyclopropenyliron compounds.[18] Part of this work has been the subject of a preliminary communication.[19]



1 a. M = Mo; R = t-Bu
b. M = Mo; R = Ph
c. M = W; R = t-Bu



2 M = Cr, Mo, W; R = H, Me;
R' = alkyl, phenyl



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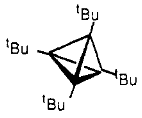

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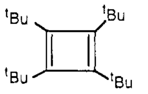

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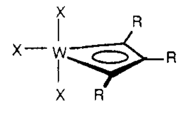

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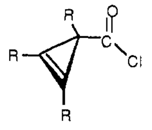

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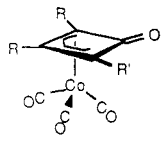
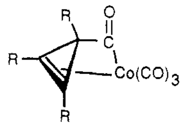
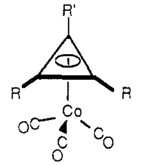


8 a. R = R' = Ph
b. R = Ph; R' = t-Bu
c. R = R' = t-Bu



9



10 a. R = R' = Ph
b. R = Ph; R' = t-Bu
c. R = R' = t-Bu

Results and Discussion

Cyclopropenyl- and (Oxocyclobutenyl)cobalt Complexes. Prior to this work all known reactions of cyclopropenyl cations with the $Co(CO)_4^-$ anion had been reported to afford exclusively the oxocyclobutenyl complexes 8.[16,20] However, Kerber had reported that the reaction of the triphenylcyclopropenyl cation **11a** with $Co_2(CO)_8$ in refluxing CH_2Cl_2 yielded both the cyclopropenyl complex **10a** and its oxocyclobutenyl relative **8a**.[17] Use of 1,2-dichloroethane (DCE) as solvent resulted in better yields of both complexes in shorter reaction times.[21] Extension of Kerber's method to other cyclopropenyl cations met with only modest success. Reaction of the unsymmetrically substituted cation **11b** with $Co_2(CO)_8$ in refluxing DCE led to formation of a mixture of cyclopropenyl complex **10b** and oxocyclobutenyl complex **8b**. Both compounds were definitively identified by their IR, mass, and NMR spectra and by microanalysis. Its ^1H and ^{13}C NMR spectra clearly identify **8b** as the illustrated, unsymmetrically substituted isomer, and no evidence for the other isomer with the alkyl group distal to the ring ketone was obtained. This selectivity also appears to be a well-established phenomenon for all reactions of cyclopropenyl cations with metal carbonyl anions.[5,16,18]

While the tri-*tert*-butylcyclopropenyl cation **11c** was unreactive toward $Co_2(CO)_8$ under these conditions, it did react slowly with the PPN^+ salt of $Co(CO)_4^-$ over a period of 1 week in refluxing THF to give moderate yields of a mixture of the cyclopropenyl complex **10c** and its oxocyclobutenyl analogue **8c**. This represents the first observation of formation of an η^3-cyclopropenyl complex of cobalt from the reaction of a cyclopropenyl cation with $Co(CO)_4^-$. Notably oxocyclobutenyl complex **8c** did not decarbonylate thermally or photochemically to give **10c** and thus cannot serve as a precursor to the cyclopropenyl compound. The only previously characterized (η^3-tri-*tert*-butylcyclopropenyl)metal complexes were those of

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(21) We are grateful to Professor R. C. Kerber for this information.

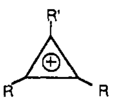
nickel.[22] These tri-*tert*-butylcyclopropenyl compounds are the closest isolobal transition-metal analogues of Maier's tetra-*tert*-butyltetrahedrane.[9] It is also noteworthy that while the bulky *tert*-butyl groups provide some steric impediment which clearly slows the rate of product formation, there is not sufficient steric crowding so as to prevent metal coordination in either the three- or four-membered ring systems.

In order to establish whether the cyclopropenylcobalt complex **10a** might serve as a precursor to an oxocyclobutenyl complex via exogenous ligand-induced ring expansion, its reactions with tertiary phosphorus ligands were explored. In refluxing benzene or toluene **10a** reacted smoothly with $P(OPh)_3$, PPh_3, or $PPhMe_2$ to give only the products of CO substitution **12a–c**. No evidence was found in the IR or NMR spectra of the crude reaction mixtures for any oxocyclobutenyl products. This substitution chemistry is analogous to that found for acyclic allyltricarbonylcobalt complexes, which undergo substitution by a dissociative pathway which is first order in cobalt and independent of phosphine concentration.[23,24] Notably, however, these latter reactions occur smoothly at 0 °C, while the cyclopropenyl analogues require elevated temperatures.

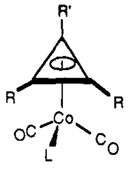
Thus it is clear that in the cobalt manifold the η^3-cyclopropenyl ligand does not undergo facile ring expansion and cannot serve as a precursor to oxocyclobutenyl complexes in the reactions of cyclopropenyl cations with $Co(CO)_4^-$. This is in contrast to the chemistry of cyclopropenyliron[18] and -molybdenum[4] analogues in which exogenous ligand-induced ring expansion has been shown to occur. A more detailed discussion of the mechanism of oxocyclobutenyl ligand formation is presented in the following paper.[18]

Cyclopropenyl- and (Oxocyclobutenyl)iron Complexes. In 1962, a report appeared in the literature on the reaction of sodium tricarbonylnitrosylferrate(1−) with triphenylcyclopropenyl chloride to give low yields of a maroon product. Two possible structures, **13a** and **14**, were considered for this material; structure **14** was considered to be most probable since chemical oxidation of the maroon product afforded triphenylcyclopropenyl tetrachloroferrate, indicating that the three-membered ring was probably still intact in the maroon complex.[25] Since **14** was isostructural with the intermediate **9** proposed by us to be the immediate precursor to oxocyclobutenyl ring formation and since reaction of the tetracarbonylcobaltate(1−) anion subsequently was shown to afford only oxocyclobutenyl complex **8a**,[16,20] a reinvestigation of the iron chemistry was undertaken.

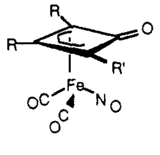
In our hands the reaction of $Na[Fe(CO)_3(NO)]$ with $[Ph_3C_3]Cl$ in THF yielded a mixture of two complexes, whose spectroscopic properties were consistent with their formulation as **13a** and **15a**. After our preliminary communication of these results,[19] Weiss et al. reported identical observations together with the crystal and molecular structure of **15a**.[26] A much cleaner reaction, to give the same products, is afforded by using the air-stable, readily available PPN^+ salt of $Fe(CO)_3(NO)^-$[27] and the BF_4^- salt of the triphenylcyclopropenyl cation. Unsymmetrically substituted cyclopropenyl cations **11b,d,e** reacted similarly with $PPN[Fe(CO)_3(NO)]$ to give mixtures of cyclopropenyl (**15b–d**) and oxocyclobutenyl (**13b–d**) complexes of iron. As in the cobalt reactions (vide supra) only the unsymmetrically substituted oxocyclobutenyl isomer was observed in these reaction mixtures. The IR spectra of **13a** and **13d** exhibited shoulders on each of the terminal CO stretching bands, indicating that two rotamers of these complexes probably exist on the IR time scale in solution. Notably reaction of the tri-*tert*-butylcyclopropenyl cation **11c** was appreciably slower than its less hindered analogues and afforded only the cyclopropenyl complex **15e** in high yields. Thus formation of cyclopropenyl complexes is a more dominant process in the reactions of $Fe(CO)_3(NO)^-$ as compared to the isoelectronic $Co(CO)_4^-$ anion.



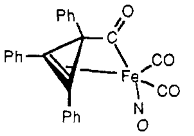
11 a. R = R' = Ph
b. R = Ph; R' = t-Bu
c. R = R' = t-Bu
d. R = Ph; R' = H
e. R = Ph; R' = Me



12 a. L = $P(OPh)_3$
b. L = PPh_3
c. L = $PPhMe_2$



13 a. R = R' = Ph
b. R = Ph; R' = H
c. R = Ph; R' = Me
d. R = Ph; R' = t-Bu



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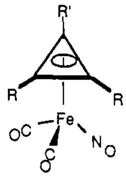
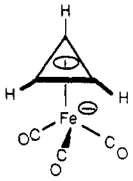


15 a. R = R' = Ph
b. R = Ph; R' = H
c. R = Ph; R' = Me
d. R = Ph; R' = t-Bu
e. R = R' = t-Bu



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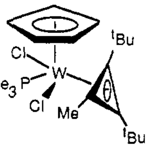

17

The cyclopropenyl complex **15b** is the first reported example of such a compound containing a hydrogen atom bound to the three-membered ring. As expected, the value of ^1J(C–H) for this bond is large (232 Hz), only slightly smaller than the values for acetylene (249 Hz) and phenylacetylene (251 Hz),[28] and indicates a high degree of s character in the C–H bond, with correspondingly higher p character in the C–C and C–Fe bonds of the strained "metallatetrahedrane" framework. It is interesting that NMR studies of ^{13}C–^{13}C coupling constants in the organic tetrahedrane 4 have demonstrated that the hybridization of the orbital from the tetrahedrane carbon site to the substituent is approximately sp in character.[9e] Our observations indicate that a similar hybridization can be used to describe the orbital from the cyclopropenyl ring carbon to hydrogen in **15b**. However, comparison with the corresponding value of ^1J(C–H) in the original diphenylcyclopropenyl cation **11d** (262 Hz) illustrates that s-character arguments must be used cautiously since overall charge also exerts a significant effect on these coupling constants.

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(29) See paragraph at end of text regarding supplementary material.

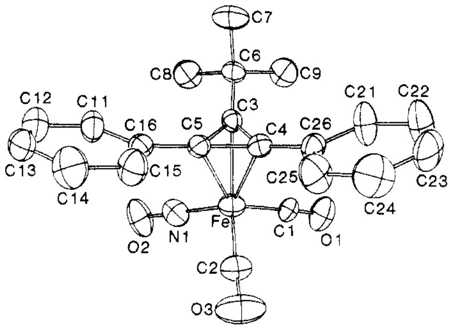


Figure 1. ORTEP drawing and atom numbering scheme for **15d**.

Table I. Crystal and Refinement Data

formula	$C_{21}H_{19}FeNO_3$
cryst system	orthorhombic
space group	*Pbca*
a, Å	8.686 (2)
b, Å	15.869 (4)
c, Å	28.53 (1)
V, Å^3	3931.6 (19)
Z	8
mol wt	389.2
ρ(calcd), g cm^{-3}	1.315
temp, °C	23
cryst dimens, mm	0.22 × 0.28 × 0.30 (red)
radiatn	graphite-monochromated Mo K$\bar{\alpha}$ (λ = 0.710 73 Å)
diffractometer	Nicolet R3
abs coeff, cm^{-1}	7.82
scan speed, deg/min	variable 4–20
2θ scan range, deg	$4 \leq 2\theta \leq 45$
scan technique	omega (full profile)
data collected	$+h,+k,+l$
std rflns	3/97 (no decay obsd)
unique data	2414 rflns (2782 collected)
unique data with $(F_o) > 2.5\sigma(F_o)$	1776
R_F, R_{wF}, GOF	0.0464, 0.0455, 1.201
highest and lowest peaks of final diff map, e Å^{-3}	0.23 and −0.23
parameters refined	236

Table II. Fractional Atomic Coordinates for $Fe(CO)_2(NO)[\eta^3\text{-}C_3(C_6H_5)_2(C_4H_9)]$ (×10^4)

atom	*x*	*y*	*z*	U_{iso}
Fe	5967 (1)	8530 (1)	1068 (1)	53 (1)*
N(1)	6151 (4)	9063 (2)	540 (1)	68 (2)*
O(1)	3210 (4)	7512 (3)	1034 (1)	89 (2)*
O(2)	6280 (5)	9423 (2)	191 (1)	97 (2)*
O(3)	5396 (5)	9749 (3)	1820 (1)	121 (2)*
C(1)	4306 (4)	7900 (3)	1052 (1)	46 (1)*
C(2)	5603 (5)	9292 (3)	1521 (2)	63 (2)*
C(3)	7599 (4)	7625 (2)	1015 (1)	40 (1)*
C(4)	7404 (5)	7810 (3)	1498 (1)	42 (1)*
C(5)	8274 (5)	8354 (2)	1218 (1)	42 (1)*
C(6)	7937 (5)	6914 (3)	686 (1)	46 (2)*
C(7)	9432 (6)	6503 (3)	856 (2)	78 (2)*
C(8)	8149 (6)	7237 (3)	186 (1)	76 (2)*
C(9)	6648 (6)	6272 (3)	685 (2)	77 (2)*
C(11)	10291 (6)	9126 (3)	783 (2)	72 (2)*
C(12)	11480 (7)	9687 (4)	759 (2)	95 (3)*
C(13)	11949 (6)	10090 (3)	1154 (3)	92 (3)*
C(14)	11241 (7)	9949 (4)	1571 (2)	97 (3)*
C(15)	10038 (6)	9374 (3)	1594 (2)	72 (2)*
C(16)	9555 (5)	8957 (3)	1199 (2)	46 (2)*
C(21)	6464 (6)	6707 (3)	2032 (2)	86 (2)*
C(22)	6185 (4)	6396 (4)	2476 (2)	114 (3)*
C(23)	6567 (7)	6865 (4)	2859 (2)	103 (3)*
C(24)	7232 (7)	7629 (4)	2801 (2)	108 (3)*
C(25)	7504 (7)	7940 (3)	2360 (2)	83 (2)*
C(26)	7127 (5)	7485 (3)	1967 (1)	51 (2)*

Table III. Selected Bond Distances and Angles for $Fe(CO)_2(NO)[\eta^3\text{-}C_3(C_6H_5)_2(C_4H_9)]$

(a) Bond Distances (Å)			
Fe–N(1)	1.735 (4)	N(1)–O(2)	1.154 (5)
Fe–C(1)	1.756 (4)	C(1)–O(1)	1.135 (5)
Fe–C(2)	1.797 (4)	C(2)–O(3)	1.135 (6)
Fe–C(3)	2.023 (4)	C(3)–C(4)	1.418 (5)
Fe–C(4)	2.090 (4)	C(4)–C(5)	1.397 (5)
Fe–C(5)	2.068 (4)	C(3)–C(5)	1.420 (5)
		C(3)–C(6)	1.498 (5)
(b) Bond Angles (deg)			
C(1)–Fe–N(1)	109.3 (2)	C(3)–C(4)–C(5)	60.6 (3)
C(2)–Fe–N(1)	108.1 (2)	C(3)–C(5)–C(4)	60.4 (3)
C(1)–Fe–C(2)	104.9 (2)	C(4)–C(3)–C(5)	59.0 (3)
Fe–N(1)–O(2)	179.4 (4)	Fe–C(2)–O(3)	177.1 (4)
Fe–C(1)–O(1)	177.7 (4)		

Crystal and Molecular Structure of 15d. Before learning of the crystallographic study of the structure of **15a**,[26] we had already determined the molecular structure of its close relative **15d** by a single-crystal X-ray diffraction study. The ORTEP drawing and labeling scheme for **15d** is presented in Figure 1. Details of the crystal and refinement data are assembled in Table I, fractional atomic coordinates are given in Table II, and selected bond distances and angles are collected in Table III. Additional crystallographic information is available as supplementary material.

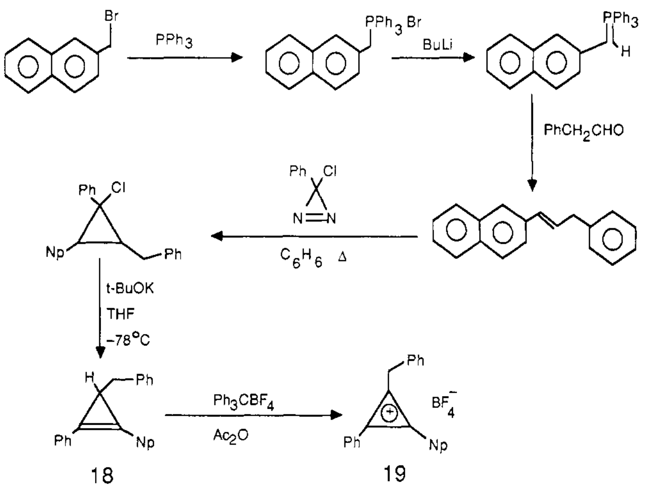
The structure of **15d** clearly reveals the η^3-cyclopropenyl–metal bonding. The metal to ring carbon distances of Fe–C(3) [2.023 (4) Å], Fe–C(4) [2.090 (4) Å], and Fe–C(5) [2.068 (4) Å] illustrate the slightly unsymmetrical coordination of the three-membered ring to the metal.

The C–C distances within the three-membered ring are virtually identical within experimental error [average 1.412 (5) Å] and are significantly shorter than the mean C–C distance within the tetrahedrane skeleton of **4** [average 1.485 (4) Å].[9d] The C–C–C angles within the cyclopropenyl ligand are all close to 60°, as expected, and as found in the tetrahedrane structure **4**.[9d] We note that the C(3)–C(6) distance of 1.498 (5) Å is identical with the corresponding distance from the tetrahedrane carbon to the quaternary carbon of the *tert*-butyl group in **4**,[9d] consistent with the idea that the orbital hybridizations within this bond are similar in both molecules. This structural observation compares favorably with the conclusion regarding hybridization in this bond reached from measurement of $^1J_{C-H}$ for compound **15b** (vide supra).

The three ring substituents are displaced from the plane of the ring, away from the metal, by 25.2° [C(6)], 16.4° [C(16)], and 14.0° [C(26)]. By way of comparison the three Ph substituents in **15a** are "bent back" by 22.5°, 18.0°, and 13.7°. The mean value of 18.5° for **15d** compares closely with that of 18.1° for **15a**. A comparison of the substituent "bend back" angles in a number of other cyclopropenyl complexes has been presented in another paper.[4] The rotational conformation of the $Fe(CO)_2(NO)$ group with respect to the three-membered ring is staggered, as predicted and as found in the structure of **15a**. Notably there is no molecular plane of symmetry in the solid-state structure of **15d**, the NO ligand lying beneath the C(3)–C(5) ring bond rather than the C(4)–C(5) bond. Such a preference in both **15a** and **15d** is difficult to rationalize on the basis of either electronic and/or steric effects (intra- and intermolecular).

Conformational and Configurational Stabilities of Cobalt and Iron Cyclopropenyl Complexes. A theoretical study of the hypothetical anion **16** at the extended Hückel level has indicated that the barrier to rotation about the metal–C_3 axis is calculated to be 6.7 kcal mol^{-1}.[30] Recently Schrock has reported that the tungsten cyclopropenyl compound **17** does not exhibit such rotation of

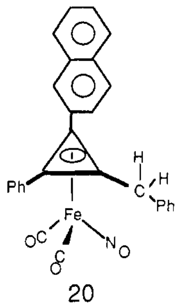
Scheme I



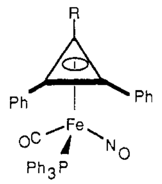
(Np = 2-Naphthyl)

the three-membered ring on the NMR scale and has suggested that this lack of fluxionality may be associated with a more "metallatetrahedrane"-like structure.[15] We have been unable to freeze out rotation of the three-membered ring in any of complexes **12** or **15a,e** at −80 °C on the ^{13}C NMR time scale, as evidenced by observation of a single resonance for the three cyclopropenyl ring carbons at this temperature. Similarly, the low-temperature ^{13}C NMR spectra of **15b–d** all show a single resonance for the two phenylated ring carbons, even though the solid-state structure of **15d** illustrates the absence of a molecular symmetry plane. These results are consistent with the low rotational energy barrier predicted by theory[30] and are identical with those observed for the molybdenum and tungsten cyclopropenyl complexes **1a** and **1c**, respectively.[4]

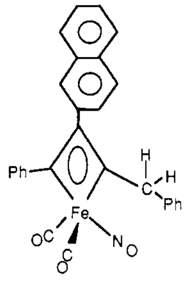
While the metallacyclobutadiene valence isomer is clearly the ground-state structure in compounds **3** and **6**, the cyclopropenyl valence isomer appears to be a readily accessible intermediate, as evidenced by carbon site scrambling on the NMR time scale and in subsequent chemistry of these compounds (see Introduction). Reasoning that in our cyclopropenyl complexes the reverse might be true and that a metallacyclobutadiene valence isomer might be a thermally accessible, albeit low concentration species in solution, we sought spectroscopic evidence by which the availability of such an isomer might be manifested. Cyclopropene **18** was synthesized by the procedure shown in Scheme I and was converted to the cyclopropenyl cation **19** by treatment with $Ph_3C^+BF_4^-$. This cation reacted with $Fe(CO)_3NO^-$ to give the cyclopropenyl complex **20**, together with a mixture of oxocyclobutenyl compounds. The latter were only identified by IR spectroscopy, and the substituent pattern on the ring was not established. A configurationally stable ground-state structure for **20** should give rise to an AB quartet for the diastereotopic benzylic protons and two ^{13}C resonances for the carbonyl carbons, even though rotation around the metal–C_3 axis is fast. However, rapid equilibrium with low concentrations of a metallacyclobutadiene valence isomer **21** would lead to rapid migration of the $Fe(CO)_2NO$ moiety from one face of the cyclopropenyl ring to the other, interconverting diastereotopic proton environments and also giving rise to a single CO environment. Experimental observations on **20** were ambiguous. The room-temperature ^1H NMR spectrum of **20** showed a singlet for the benzylic protons at 300 MHz, but the $^{13}C\{^1H\}$ NMR spectrum exhibited two carbonyl carbon resonances separated by 4 Hz. The spectra were invariant from −60 to +60 °C. It is difficult to visualize a dynamic process whereby the CO ligands remain diastereotopic but the benzylic proton environments are scrambled, so we conclude that the molecule is conformationally rigid but that unfortunately the CH_2 protons are accidentally isochronous. This conclusion is supported by NMR observations on complexes **22**, which both show three resonances for the cyclopropenyl ring carbons at +60 °C. Any fast isomerization via a ferracyclobutadiene intermediate would serve to scramble the environments of the phenyl-substituted cyclopropenyl ring carbon atoms in **22**.[47] The absence of coalescence of the CO resonances of **20** at +60 °C allows an estimate of 17 kcal·mol^{-1} to be made as the lower limit of E_a for isomerization of **20** to **21**.



20



22



21

It seems clear, therefore, that metallacyclobutadiene intermediates are not accessible on the NMR time scale in these systems.

Experimental Section

General Procedures. Reactions were carried out in conventional oven-dried Schlenck glassware under an atmosphere of dinitrogen which was deoxygenated over BASF catalyst and dried over P_4O_{10} or in a Vacuum Atmospheres glovebox equipped with a HE-493 gas purification system. Hydrocarbon and ethereal solvents were dried by distillation from sodium or potassium benzophenone ketyl. Acetonitrile, 1,2-dichloroethane, and methylene chloride were distilled from P_4O_{10}. All solvents were stored and transferred under purified dinitrogen.

The 300-MHz ^1H, 75-MHz $^{13}C\{^1H\}$, and 121-MHz $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian XL-300 spectrometer; chemical shifts for ^1H and ^{13}C resonances are reported in parts per million downfield from internal tetramethylsilane. Chemical shifts for $^{31}P\{^1H\}$ spectra were referenced in parts per million upfield relative to 85% H_3PO_4 by measurement of the $^{31}P\{^1H\}$ spectrum of trimethyl phosphite under identical conditions and taking the chemical shift of $P(OMe)_3$ to be +141.0 ppm.[43] Infrared spectra were recorded on a Perkin-Elmer 599 spectrometer and calibrated against the 1601 cm^{-1} peak of polystyrene. Electron-impact (70-eV) mass spectra were run on a Finnegan 4023 spectrometer, and positive ion fast atom bombardment (FAB) mass spectra were recorded at the NSF Middle Atlantic Regional Mass Spectrometry Facility at the John Hopkins School of Medicine, Baltimore, MD.

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(31) Compounds **22** were prepared as described in the following paper.[18]

Starting Materials. Benzamidine hydrochloride hydrate, phenylacetaldehyde, phenylacetylene, *trans*-β-methylstyrene, 2-(bromomethyl)naphthalene, *n*-butyllithium (1.6 M in hexane), trimethyloxonium tetrafluoroborate, iodomethane, triphenylphosphine, and bis(triphenylphosphine)nitrogen chloride, [PPN]Cl (PPN = $Ph_3P{=}N{=}PPh_3$), were purchased from Aldrich Chemical Co. and were used without further purification. Tetrafluoroboric acid (aqueous, 48–50%), α,α-dichlorotoluene, and triphenyl phosphite were purchased from Eastman Kodak Co. and were used without further purification. Diphenylacetylene was purchased from either Aldrich Chemical Co. or Eastman Kodak and used without further purification. Dimethylphenylphosphine and octacarbonyldicobalt were obtained from Strem Chemical and used as purchased. 3,3-Dimethyl-1-butyne was used as purchased from Farchan Chemical Co. Phenylchlorodiazirine,[32] 1-phenyl-3,3-dimethyl-1-butyne,[33] triphenylcarbenium tetrafluoroborate, and 1,2-diphenyl-3-methylcyclopropene[32] were prepared by literature procedures. Diphenylmethylcyclopropenyl tetrafluoroborate was prepared from 1,2-diphenyl-3-methylcyclopropene according to published procedures.[35] Tri-*tert*-butylcyclopropenyl tetrafluoroborate was prepared by literature procedures.[42] Bis(triphenylphosphine)nitrogen nitrite ($[PPN][NO_2]$),[36] bis(triphenylphine)nitrogen tricarbonylnitrosylferrate ($[PPN][Fe(CO)_3NO]$),[27] and sodium tricarbonylnitrosylferrate[37] were prepared according to literature procedures.

Triphenylcyclopropenyl chloride ($[C_3Ph_3]Cl$) was prepared according to the method of Breslow.[38]

Triphenylcyclopropenyl Tetrafluoroborate ($[C_3Ph_3][BF_4]$). The bis(triphenylcyclopropenyl) ether was prepared by the method of Breslow[38] and isolated as a crude yellow solid. In a typical preparation, this solid (26 g, 0.11 mmol) was redissolved in Et_2O (1400 mL), cooled to −15 °C, and treated with a solution of HBF_4 (63.4 g, 0.354 mol) in acetic anhydride (361 g, 3.52 mol). The tan precipitate that formed was filtered, dried, and recrystallized from hot acetonitrile to afford white needles of the cyclopropenyl salt. The mother liquor was twice concentrated and cooled to 0 °C to induce crystallization of second and third crops. The total yield of recrystallized product was 26 g (58%).

Diphenylcyclopropenyl Tetrafluoroborate ($[C_3Ph_2H][BF_4]$) and *tert*-Butyldiphenylcyclopropenyl Tetrafluoroborate ($[C_3Ph_2\text{-}t\text{-}Bu][BF_4]$) were prepared by addition of phenylchlorocarbene from phenylchlorodiazirine to the appropriate alkyne by modifications of the general method of Padwa.[39]

The diphenylcyclopropenyl cation was prepared as follows. A mixture of phenylchlorodiazirine (approximately 0.072 mol) and phenylacetylene (5.48 g, 0.0634 mol) in dry benzene (500 mL) was refluxed 3.5 h. After cooling, the solvent was removed on a rotary evaporator, leaving a yellow oil. The oil was taken up in Et_2O (600 mL), and 5% $NaHCO_3$(aq) (200 mL) was added to ensure conversion to the bis(cyclopropenyl) ether.[40] This mixture was stirred (30 min), the layers were separated, and the organic layer was dried over $MgSO_4$. After filtration, the solution of the bis(cyclopropenyl) ether was cooled to 0 °C and treated dropwise with a solution of 49% aqueous HBF_4 (22.8 g, 0.127 mol) in acetic anhydride (129.6 g, 1.27 mol). The tan precipitate was filtered and dried in vacuo to yield the product as an off-white powder (5.2 g, 0.019 mol, 30%) which could be recrystallized from warm acetonitrile/benzene[41] to yield white needles. However, the recovery from recrystallization was low (less than 50%), and the crude cyclopropenyl salt was used successfully in reactions with $Fe(CO)_3NO^-$.

The *tert*-butyldiphenylcyclopropenyl cation was prepared in a similar fashion. A mixture of phenylchlorodiazirine (approximately 0.072 mol) and 3,3-dimethyl-1-phenyl-1-butyne (10.0 g, 0.0634 mol) in dry benzene (500 mL) was refluxed 3.5 h. After cooling, the solvent was removed on a rotary evaporator and the residue was taken up in Et_2O (500 mL) and treated with a 5% aqueous $NaHCO_3$ (200 mL) for 30 min. The layers were separated, and the organic layer was dried over $MgSO_4$ and filtered. The ether solution was cooled to 0 °C and treated dropwise with a solution of 49% aqueous HBF_4 (22.8 g, 0.127 mol) in acetic anhydride (129.6 g, 1.27 mol). The white precipitate was filtered and dried in vacuo, leaving the cyclopropenyl salt as a white powder (10.5 g, 0.031 mol, 50%). The crude salt was recrystallized from hot methanol to yield white plates (7.52 g). A second crop was obtained by reducing the volume of the mother liquor by half, adding Et_2O until the cloud point was reached, and then cooling to −25 °C. The total yield was 8.1 g (38%).

Reaction of $Co_2(CO)_8$ with $[C_3Ph_3][BF_4]$. A mixture of $Co_2(CO)_8$ (3.41 g, 9.96 mmol) and $[C_3Ph_3][BF_4]$ (2.53 g, 7.15 mmol) in deoxygenated 1,2-dichloroethane (100 mL) was refluxed (12 h). The solvent was removed in vacuo [along with some unreacted $Co_2(CO)_8$], and the residue was chromatographed on an alumina (neutral, activity I)/hexanes (22 × 300 mm) column. Hexanes first eluted a mixture of unreacted $Co_2(CO)_8$ and $Co_4(CO)_{12}$, identified by IR, and then a small amount of the bridging acetylene complex $[Co_2(CO)_6(PhC{\equiv}CPh)]$ also identified by IR[17] but not otherwise characterized. Hexane next eluted a yellow band which, after removal of solvent in vacuo, afforded a yellow solid identified as $Co(\eta^3\text{-}C_3Ph_3)(CO)_3$[17] (**10a**; 1.7 g, 4.1 mmol, 57%). Et_2O eluted $Co(\eta^3\text{-}C_3Ph_3CO)(CO)_3$ (**8a**) which was also isolated as a yellow solid (1.3 g, 2.9 mmol, 41%) and identified by comparison of IR data with literature data.[17]

Reaction of $Co_2(CO)_8$ with $[C_3Ph_2\text{-}t\text{-}Bu][BF_4]$. A mixture of $Co_2(CO)_8$ (2.27 g, 6.64 mmol) and $[C_3Ph_2\text{-}t\text{-}Bu][BF_4]$ (1.59 g, 4.77 mmol) in deoxygenated 1,2-dichloroethane (50 mL) was refluxed 4 h. The solvent was removed in vacuo and the residue chromatographed on an Alumina (neutral, activity I)/hexanes column (19 × 250 mm). Hexanes eluted $Co(\eta^3\text{-}C_3Ph_2\text{-}t\text{-}Bu)(CO)_3$ (**10b**) which was isolated as a yellow crystalline solid (0.259 g, 0.664 mmol, 14%). This material was recrystallized from hexanes (0 °C) to afford **10b** as yellow cubes: mp 95–96 °C dec; IR (hexane) ν_{CO} 2050, 1988 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 7.6–7.2 (m, Ph, 10 H), 1.37 (s, *t*-Bu, 9 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 132.7, 128.8 (br), 127.5 (Ph), 111.9 (*C*-*t*-Bu), 103.3 (*C*Ph), 31.6 (*C*Me$_3$), 30.1 (CH_3) (metal carbonyl resonances not observed); MS (FAB), *m/e* 390 (P^+), 362 (P^+ − CO), 334 (P^+ − 2CO), 307 (P^+ − 3CO), 247 ($C_3Ph_2\text{-}t\text{-}Bu^+$). Anal. Calcd for $C_{22}H_{19}CoO_3$: C, 67.70; H, 4.91. Found: C, 67.62; H, 4.96.

Et_2O then eluted a second yellow band which, after removal of solvent in vacuo, afforded a yellow solid identified as $Co(\eta^3\text{-}C_3Ph_2\text{-}t\text{-}BuCO)(CO)_3$ (**8b**: 0.816 g, 1.95 mmol, 41%). Crystallization from MeOH yielded **8b** as yellow cubes: mp 125–128 °C dec; IR (hexane) ν_{CO} 2073, 2025, 2009, $\nu_{C=O}$ 1716 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 7.7–7.1 (m, Ph, 10 H), 1.23 (s, *t*-Bu, 9 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 199.4 (br, CO), 166.3 (C=O), 131.7, 130.5, 128.7, 128.5 (br), 127.1 (Ph), 110.7 (*C*-*t*-Bu), 94.8 (*C*Ph), 92.3 (*C*Ph), 32.9 (*C*Me$_3$), 28.8 (CH_3); MS (FAB), *m/e* 419 (P^+), 391 (P^+ − CO), 363 (P^+ − 2CO), 334 (P^+ − 3CO), 247 ($C_3Ph_2\text{-}t\text{-}Bu^+$). Anal. Calcd for $C_{23}H_{19}CoO_4$: C, 66.04; H, 4.58. Found: C, 65.92; H, 4.62.

Reaction of $[PPN^+][Co(CO)_4]$ with $[t\text{-}Bu_3C_3][BF_4]$. A mixture of $PPN^+Co(CO)_4^-$ (2.41 g, 3.4 mmol) and $[t\text{-}Bu_3C_3]BF_4$ (1.00 g, 3.4 mmol) in THF (75 mL) was refluxed for 7 days and then allowed to cool. The mixture was filtered, and the filtrate

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was evaporated under water aspirator vacuum. The residue was chromatographed on an alumina/hexanes column (activity III, 20 × 200 mm). Elution with hexanes gave a very pale yellow band which was evaporated. Crystallization of the residue from hexanes gave $Co(\eta^3\text{-}t\text{-}Bu_3C_3)(CO)_3$ (**10c**) as white crystals (0.73 g, 30%): mp 109–111 °C dec; IR (hexanes) ν_{CO} 2044, 1985 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (s, *t*-Bu); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 71.2 (*C*-*t*-Bu), 31.1 (C*Me*$_3$), 30.9 (*C*Me$_3$), metal carbonyls not observed. Anal. Calcd for $C_{18}H_{27}CoO_3$: C, 61.71; H, 7.77. Found: C, 61.60; H, 7.81. Further elution with hexanes gave a second pale yellow band which was evaporated in vacuo. Crystallization of the residue from hexanes afforded $Co(\eta^3\text{-}t\text{-}Bu_3C_3CO)(CO)_3$ (**8c**) as pale yellow crystals (0.77 g, 29%): mp 85–87 °C dec; IR (hexanes) ν_{CO} 2064, 2020, 2004, $\nu_{C=O}$ 1711 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36 (s, 18 H, *t*-Bu), 1.32 (s, 9 H, *t*-Bu); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 200.7 (CoCO), 170.0 (*C*=O), 110.0 (*C*-*t*-Bu), 107.5 (*C*-*t*-Bu), 33.4 (*C*Me$_3$), 33.2 (C*Me*$_3$), 32.4 (*C*Me$_3$), 30.5 (C*Me*$_3$). Anal. Calcd for $C_{19}H_{27}CoO_4$: C, 60.31; H, 7.19. Found: C, 60.26; H, 7.22.

Reaction of $Co(\eta^3\text{-}C_3Ph_3)(CO)_3$ (10a) with Triphenyl Phosphite [$P(OPh)_3$]. A mixture of **10a** (0.80 g, 1.95 mmol) and $P(OPh)_3$ (0.63 g, 2.1 mmol) in dry, deoxygenated benzene (20 mL) was refluxed (8 h). The solvent was removed in vacuo, and the residue was chromatographed on a Florisil/hexanes column (22 × 300 mm). Hexanes/Et_2O (2:1) eluted a yellow band which began to crystallize in the column. Acetone was used to completely elute the yellow band which, after removal of solvent, afforded yellow crystals identified as $Co(\eta^3\text{-}C_3Ph_3)(CO)_2[P(OPh)_3]$ (**12a**; 1.25 g, 1.80 mmol, 93%). Recrystallization from hot acetonitrile afforded **12a** as yellow needles: mp 165–166 °C dec; IR (CH_2Cl_2) ν_{CO} 2020, 1979 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 8.0–6.6 (m, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 151.4 (d, ipso Ph, J_{PC} = 7 Hz), 134.0, 129.1 (br), 124.2 (br), 121.3 (br) (Ph), 48.3 (d, *C*Ph, J_{PC} = 6 Hz) (metal carbonyl resonances not observed); MS (FAB), *m*/*e* 693 (P^+), 664 (P^+ – CO), 636 (P^+–2CO), 327 (P^+–2CO – $P(OPh)_3$), 267 ($C_3Ph_3^+$). Anal. Calcd for $C_{41}H_{30}CoO_5P$: C, 71.10; H, 4.36. Found: C, 71.04; H, 4.43.

Reaction of $Co(\eta^3\text{-}C_3Ph_3)(CO)_3$ (10a) with Triphenylphosphine (PPh_3). A mixture of **10a** (0.35 g, 0.85 mmol) and PPh_3 (0.25 g, 0.94 mmol) in dry, deoxygenated toluene (20 mL) was refluxed (5 h). After cooling, the mixture was filtered and the solvent was removed in vacuo, leaving a yellow solid (0.521 g, 0.807 mmol, 95%) identified as $Co(\eta^3\text{-}C_3Ph_3)(CO)_2(PPh_3)$ (**12b**). The crude product was recrystallized from Et_2O/hexanes to yield **12b** as yellow needles: mp 183 °C dec; IR (CH_2Cl_2) ν_{CO} 1992, 1942 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 7.6–7.2 (m, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 206.8 (br, CoCO), 135.5–126.3 (20 lines, Ph), 46.8 (d, *C*Ph, J_{PC} = 2 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 48.1 (br). Anal. Calcd for $C_{41}H_{30}CoO_2P$: C, 76.40; H, 4.69. Found: C, 76.56; H, 4.76.

Reaction of $Co(\eta^3\text{-}C_3Ph_3)(CO)_3$ (10a) with Dimethylphenylphosphine (PMe_2Ph). A mixture of **10a** (0.648 g, 1.58 mmol) and PMe_2Ph (0.24 mL, 1.73 mmol) in dry, deoxygenated benzene (30 mL) was refluxed 9 h. The IR of the crude reaction mixture showed only terminal metal–CO bands, indicating that no oxocyclobutenyl complex had formed. The solvent was removed in vacuo, and the residue, after being redissolved in the minimum amount of Et_2O, was filtered through a plug of Florisil with additional Et_2O. The solvent was removed in vacuo, leaving $Co(\eta^3\text{-}C_3Ph_3)(CO)_2(PMe_2Ph)$ (**12c**) as an air-sensitive yellow oil (0.80 g, 1.53 mmol, 97%). Attempts to recrystallize **12c** resulted in precipitation of a yellow powdery solid at –60 °C which became an oil on drying in vacuo and warming to room temperature: IR (CH_2Cl_2) ν_{CO} 1994, 1945 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 7.8–7.0 (m, Ph, 20 H), 1.46 (d, PCH_3, 6 H, J_{PH} = 7 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 135.3, 128.4 (br), 126.2 (br, Ph), 46.1 (br, *C*Ph), 17.6 (br, PCH_3) (metal carbonyl resonances not observed). Satisfactory microanalysis results could not be obtained for this material, even though it was spectroscopically pure.

Reaction of $[C_3Ph_3]Cl$ with $Na[Fe(CO)_3NO]$. A suspension of $Na[Fe(CO)_3NO]$ (0.526 g, 2.72 mmol) and $[C_3Ph_3]Cl$ (0.75 g, 2.48 mmol) in deoxygenated MeOH (20 mL) was stirred for 16 h. The solvent was removed in vacuo, leaving a brown oily solid which was chromatographed on a Florisil column (19 × 300 mm) packed with hexanes. Hexane eluted a red band which, after removal of solvent under reduced pressure, afforded a red solid identified as $Fe(\eta^3\text{-}C_3Ph_3)(CO)_2(NO)$ (**15a**: 0.32 g, 0.78 mmol, 31%). Recrystallization from hexane yielded pure **15a**: mp 129 °C dec; IR (hexane) ν_{CO} 2033, 1992, ν_{NO} 1760 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 8.7–6.6 (m, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 213.0 (CO), 131.8, 129.2, 128.8, 128.3 (Ph), 54.9 (*C*Ph); MS (EI, 70 eV), *m*/*e* 409 (P^+), 381 (P^+ – 2CO), 323 (P^+ – 2CO – NO), 267 ($C_3Ph_3^+$). Anal. Calcd for $C_{23}H_{15}FeNO_3$: C, 67.51; H, 3.69; N, 3.42. Found: C, 67.35; H, 3.68; N, 3.38.

Hexane/Et_2O (4:1) eluted an orange-red band which, after removal of solvent in vacuo, yielded an orange-red solid identified as $Fe(\eta^3\text{-}C_3Ph_3CO)(CO)_2(NO)$ (**13a**; 0.20 g, 0.46 mmol, 19%): mp 125 °C dec; IR (hexanes) ν_{CO} 2060 (sh), 2053, 2025 (sh), 2016, ν_{NO} 1798, $\nu_{C=O}$ 1720 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 8.3–6.5 (m, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 210.41 (CO), 164.6 (C=O), 132.3, 131.0, 128.6 (br, Ph), 100.4 (*C*Ph), 94.8 (*C*Ph). Microanalytical data for this complex have been reported elsewhere.[26]

Reaction of $[C_3Ph_3][BF_4]$ with $[PPN][Fe(CO)_3NO]$. Solid $[C_3Ph_3][BF_4]$ (1.77 g, 5.00 mmol) was added all at once to a stirring solution of $[PPN][Fe(CO)_3NO]$ (3.54 g, 5.00 mmol) in dry, deoxygenated CH_2Cl_2 (50 mL). The mixture turned red immediately and was allowed to stir overnight (12 h). The solvent was removed in vacuo, and the residue was chromatographed on a Florisil/hexanes column as above to afford **15a** (0.727 g, 1.78 mmol, 36%) and **13a** (1.14 g, 2.61 mmol, 52%). This reaction was much cleaner and affords greater overall yield of products (88% vs. 50%) compared with the reaction of the sodium salt of tricarbonylnitrosylferrate(1–).

Reaction of $[C_3Ph_2H][BF_4]$ with $[PPN][Fe(CO)_3NO]$. Solid $[C_3Ph_2H][BF_4]$ (4.54 g, 16.3 mmol) was added all at once to a yellow stirring solution of $[PPN][Fe(CO)_3NO]$ (11.6 g, 16.3 mmol) in dry, deoxygenated CH_2Cl_2 (125 mL). The mixture became red immediately and was allowed to stir (20 h). The solvent was removed in vacuo and the residue chromatographed on a Florisil column (46 × 200 mm) packed with hexanes. Hexanes eluted a red band which, after removal of the solvent in vacuo, yielded a red solid identified as $Fe(\eta^3\text{-}C_3Ph_2H)(CO)_2NO$ (**15b**; 0.340 g, 1.02 mmol, 6%). Recrystallization from hexane (–50 °C) yielded air-sensitive red crystals: mp 100–101 °C dec; IR (hexane) ν_{CO} 2035, 1992; ν_{NO} 1765 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 7.6–7.2 (m, Ph, 10 H), 5.25 (s, C H, 1 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 213.2 (CO), 131.4–128.1 (7 lines, poorly resolved, Ph), 51.9 (*C*Ph), 36.5 (CH); ^{13}C NMR ($CDCl_3$, 20 °C, C–H coupled spectrum) δ 213.0 (CO), 131.4–127.1 (complex m, Ph), 51.9 (s, *C*Ph), 36.5 (d, CH, J_{CH} = 232 Hz); MS (FAB), *m*/*e* 333 (P^+), 305 (P^+ – CO), 277 (P^+ – 2CO), 247 (P^+ – 2CO – NO), 191 ($C_3Ph_2H^+$). Anal. Calcd for $C_{17}H_{11}FeNO_3$: C, 61.29; H, 3.33; N, 4.20. Found: C, 61.07; H, 3.43; N, 4.10.

Ether then eluted an orange red band which, after removal of solvent in vacuo, afforded an air-sensitive, red, glassy solid identified as $Fe(C_3Ph_2HCO)(CO)_2(NO)$ (**13b**; 3.08 g, 8.53 mmol, 52%). Attempts to recrystallize **13b** invariably led to oils or decomposition:[48] IR (hexane) ν_{CO} 2050, 2010, ν_{NO} 1801, $\nu_{C=O}$ 1736 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 7.98–6.78 (m, Ph, 10 H), 5.50 (s, CH, 1 H); $^{13}C\{^1H\}$ NMR (acetone-d_6, 20 °C) δ 212.6, 211.6 (CO), 166.2 (C=O), 133.2, 131.9, 131.3, 130.3, 129.7, 129.5, 129.3, 128.6 (Ph), 103.7 (*C*Ph), 90.2 (*C*Ph), 75.6 (*C*H); MS (EI, 70 eV), *m*/*e* 333 (P^+ – CO), 305 (P^+ – 2CO), 275 (P^+ – 2CO – NO), 220 (C_3 – Ph_2HCO^+), 191 ($C_3Ph_2H^+$).

Reaction of $[C_3Ph_2Me][BF_4]$ with $[PPN][Fe(CO)_3NO]$. Solid $[C_3Ph_2Me][BF_4]$ (1.46 g, 5.00 mmol) was added all at once to a yellow, stirring solution of $[PPN][Fe(CO)_3NO]$ (3.54 g, 5.00 mmol) in dry, deoxygenated CH_2Cl_2 (40 mL). The mixture became deep red immediately and was allowed to stir at room temperature (24 h). The solvent was removed, and the residue was chromatographed on a Florisil column (22 × 300 mm) packed with hexanes. Hexane eluted a red band which, after evaporation of solvent under reduced pressure, yielded $Fe(\eta^3\text{-}C_3Ph_2Me)(CO)_2NO$ (**15c**). Hexane/CH_2Cl_2 (4:1) eluted the last traces of **15c**. The fractions were combined. The solvents were removed in vacuo to give **15c** as a red solid (1.13 g, 3.25 mmol, 65%) which could be recrystallized from MeOH (–40 °C) to afford red crystals: mp 98 °C dec; IR (hexane) ν_{CO} 2024, 1981, ν_{NO} 1751 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 7.5–7.1 (m, Ph, 10 H), 2.41 (s, CH_3, 3 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 213.8 (CO), 131.9, 128.9, 128.2 (Ph), 55.7 (*C*Ph), 53.6 (*C*Me), 10.7 (CH_3); MS (FAB), *m*/*e* 319 (P^+ – CO), 291 (P^+ – 2CO), 205 ($C_3Ph_2Me^+$). Anal. Calcd for $C_{18}H_{13}FeNO_3$: C, 62.28; H, 3.77; N, 4.03. Found: C, 62.23; H, 3.82; N, 3.99. Et_2O

eluted a red-orange band which, after removal of solvent in vacuo, yielded a red oil identified as Fe(η^3-C$_3$Ph$_2$MeCO)(CO)$_2$(NO) (**13c**: 0.279 g, 0.744 mmol, 15%). Attempts to recrystallize this material led only to slightly impure orange powders with low recovery:[48] IR (CH$_2$Cl$_2$) ν_{CO} 2051, 2012, ν_{NO} 1786, $\nu_{C=O}$ 1701 cm^{-1}; ^{1}H NMR (CDCl$_3$, 20 °C) δ 8.0–6.5 (m, Ph, 10 H), 2.24 (s, CH$_3$, 3 H); ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C) δ 211.7, 211.2 (CO), 167.1 (C=O), 135.5–119.0 (br, m, Ph), 102.9, 94.3 (*C*Ph), 65.7 (*C*Me), 11.0 (CH$_3$).

Reaction of [C$_3$Ph$_2$-*t*-Bu][BF$_4$] with [PPN][Fe(CO)$_3$NO]. Solid [C$_3$Ph$_2$-*t*-Bu][BF$_4$] (1.67 g, 5.00 mmol) was added to a stirring yellow solution of [PPN][Fe(CO)$_3$NO] (3.54 g, 5.00 mmol) in dry, deoxygenated CH$_2$Cl$_2$ (75 mL). The mixture immediately became deep red and was allowed to stir (1 h). The solvent was removed in vacuo, and the residue was chromatographed on a Florisil column (19 × 250 mm) packed with hexanes. Hexane eluted a red band which, after removal of solvent, afforded deep red crystals identified as Fe(η^3-C$_3$Ph$_2$-*t*-Bu)(CO)$_2$NO (**15d**; 1.24 g, 3.19 mmol, 64%). Recrystallization from hexane at −50 °C yielded translucent red cubes: mp 111–113 °C dec; IR (hexane) ν_{CO} 2025, 1981, ν_{NO} 1747 cm^{-1}; ^{1}H NMR (CDCl$_3$, 20 °C) δ 7.7–7.2 (m, Ph, 10 H), 1.45 (s, *t*-Bu, 9 H); ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C) δ 214.0 (CO), 131.7, 129.4, 128.7, 128.0 (Ph), 67.2 (*C*Ph), 57.5 (*C*-*t*-Bu), 32.7 (*C*Me$_3$), 30.5 (C*Me*$_3$); MS (FAB), *m/e* 389 (P$^+$), 361 (P$^+$ − CO), 333 (P$^+$ − 2CO), 303 (P$^+$ − 2CO − NO), 247 (C$_3$Ph$_2$-*t*-Bu$^+$). Anal. Calcd for C$_{21}$H$_{19}$FeNO$_3$: C, 64.80; H, 4.92; N, 3.60. Found: C, 64.76; H, 4.94; N, 3.57. A single crystal was selected for X-ray structure analysis (see below). Et$_2$O eluted a red orange band which, after removal of solvent, yielded a red solid identified as Fe(η^3-C$_3$Ph$_2$-*t*-BuCO)(CO)$_2$(NO) (**13d**; 0.462 g, 1.11 mmol, 22%). Recrystallization from MeOH afforded **13d** as red cubes: mp 100 °C dec; IR (hexane) ν_{CO} 2055 (sh), 2045, 2021 (sh), 2005, ν_{NO} 1794, 1775 (sh), $\nu_{C=O}$ 1713 cm^{-1}; ^{1}H NMR (CDCl$_3$, 20 °C) δ 8.8–8.1 (m, Ph), 2.48 (s, *t*-Bu); ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C) δ 212.7, 210.7 (CO), 160.6 (C=O), 131.7, 131.0, 130.2, 129.5, 129.1, 128.9, 127.6, 126.9 (Ph), 112.9 (*C*Ph), 104.0 (*C*Ph), 95.8 (*C*-*t*-Bu), 33.7 (*C*Me$_3$), 29.8 (C*Me*$_3$). Anal. Calcd for C$_{22}$H$_{19}$FeNO$_4$: C, 63.33; H, 4.59; N, 3.36. Found: C, 63.40; H, 4.63; N, 3.32.

Reaction of [C$_3$-*t*-Bu$_3$][BF$_4$] with [PPN][Fe(CO)$_3$NO]. A mixture of [PPN][Fe(CO)$_3$NO] (1.20 g, 1.7 mmol) and [C$_3$-*t*-Bu$_3$][BF$_4$] (0.50 g, 1.7 mmol) in THF (50 mL) was refluxed for 5 h, then cooled, and evaporated to dryness. The residue was extracted with hexanes until no more orange solution was obtained, and the extracts were filtered through a short Florisil plug. The filtrate was evaporated to dryness and the residue recrystallized from hexanes (−60 °C) to give Fe(η^3-C$_3$-*t*-Bu$_3$)(CO)$_2$NO (**15e**) as orange crystals (0.55 g, 95%): mp 155 °C dec; IR (hexanes) ν_{CO} 2019, 1974, ν_{NO} 1749 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.26 (s, *t*-Bu); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 217.5 (FeCO), 75.9 (*C*-*t*-Bu), 31.9 (*C*Me$_3$), 31.4 (C*Me*$_3$). Anal. Calcd for C$_{17}$H$_{27}$FeNO$_3$: C, 58.46; H, 7.79; N, 4.01. Found: C, 58.54; H, 7.83; N, 3.98.

1-(2-Naphthyl)-3-phenyl-1-propene was prepared by a modification of the general method of Johnson and Kyllingstad.[45] A mixture of 2-(bromomethyl)naphthalene (25.0 g, 0.113 mol) and PPh$_3$ (29.7 g, 0.113 mol) in dry benzene (250 mL) was refluxed (15 h). The crude phosphonium bromide was filtered, dried, and recrystallized from CHCl$_3$/benzene to yield white crystals of (2-naphthylmethyl)triphenylphosphonium bromide (53.3 g, 0.100 mol, 97.5%). To a slurry of the phosphonium bromide (24.2 g, 50.0 mmol) in dry benzene was added *n*-BuLi (29.4 mL of a 1.7 M solution in hexanes, 50.0 mmol) via syringe. The mixture became deep red and was allowed to stir (1 h). Phenylacetaldehyde (6.01 g, 50.0 mmol) was then added and the mixture stirred (16 h) at room temperature. To this mixture was added 40% NaHSO$_3$(aq) (400 mL). The layers were separated, and the organic layer was dried over MgSO$_4$ and then filtered. The solvent was removed on a rotary evaporator, and the crude yellow, oily solid (18.8 g) was chromatographed on a silica column (200 g) packed with hexanes. Hexane eluted first a small amount of a white solid (0.26 g) which was not identified. Hexane next eluted 1-(2-naphthyl)-3-phenyl-1-propene which was isolated as a yellow oil (4.71 g, 19.3 mmol, 39%) and identified by comparison of its IR spectrum to literature data.[46]

1-(2-Naphthyl)-2-phenyl-3-benzylcyclopropene (18) was prepared according to the general method of Padwa and coworkers.[32] A solution of the olefin **115** (2.5 g, 10.2 mmol) and phenylchlorodiazirine (38.8 mL of a 0.29 M solution in benzene, 11.2 mmol) in benzene (200 mL) was refluxed (4 h). After cooling, the solvent was removed on a rotary evaporator and the residue was filtered through a column of silica gel (21 × 150 mm) with Et$_2$O (~150 mL). The filtrate was collected and the solvent was removed. The residue was taken up in dry THF (250 mL) and cooled to −78 °C under N$_2$. Dry, powdered KO-*t*-Bu (4.6 g, 40.8 mmol) was added all at once, and the mixture was allowed to stir at −78 °C (1 h) and then warmed to room temperature overnight (12 h). The mixture was warmed to 65 °C (3 h) and then cooled, and H$_2$O (25 mL) was added dropwise. The solvent was removed on a rotary evaporator, leaving a brown oil. The residue was taken up in Et$_2$O (150 mL), the layers were separated, and the Et$_2$O layer was washed with H$_2$O (5 × 50 mL). The organic layer was dried over MgSO$_4$, filtered, and the solvent was removed on a rotary evaporator. The yellow oily residue was chromatographed on a silica gel column (22 × 370 mm) packed with hexanes. Hexane eluted a yellow band which, after removal of solvent under reduced pressure, yielded a yellow solid (1.9 g, 15.72 mmol, 56%) identified spectroscopically as the cyclopropene **18**: ^{1}H NMR (CDCl$_3$, 20 °C) δ 7.9–7.2 (m, aromatic, 17 H), 3.15 (dd, CH_aH$_b$Ph, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 5 Hz), 3.03 (dd, CH$_a$$H_b$Ph, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 5 Hz) (2 H total), 2.64 (t, C*H*, $^3J_{HH}$ = 5 Hz, 1 H).

Benzyl(2-naphthyl)phenylcyclopropenyl tetrafluoroborate (19) was prepared by adding a saturated solution of [Ph$_3$C][BF$_4$] in acetic anhydride to a stirring solution of the cyclopropene **18** (1.5 g, 4.5 mmol) until the intense yellow color of the trityl cation was no longer discharged. The mixture was stirred (15 min), and Et$_2$O (600 mL) was added to complete precipitation of the cyclopropenyl cation. The precipitate was filtered, and the cyclopropenyl salt **19** (1.03 g, 2.46 mmol) was dried in vacuo and used without further purification: IR (KBr) 3050 (w), 1625 (m), 1595 (m), 1497 (m), 1475 (m), 1420 (s, br), 1381 (m), 1050 (s, br), 750 (m), 705 (m) cm^{-1}.

Reaction of [C$_3$(CH$_2$Ph)(Ph)(2-Np)]BF$_4$ (19) with [PPN][Fe(CO)$_3$NO]. Solid [C$_3$(CH$_2$Ph)(Ph)(2-Np)][BF$_4$] (1.03 g, 2.46 mmol) was added to a yellow, stirring solution of [PPN]-[Fe(CO)$_3$NO] (1.74 g, 2.46 mmol) in dry, deoxygenated CH$_2$Cl$_2$ (20 mL). The resulting mixture was stirred (18 h) at room temperature, and the solvent was removed *in vacuo*. The residue was chromatographed on a Florisil/hexanes column (22 × 150 mm). Hexane eluted a red band which, after removal of solvent, yielded a red oil identified as Fe[η^3-C$_3$(CH$_2$Ph)(Ph)(Np)](CO)$_2$(NO) (**20**; 0.35 g, 0.74 mmol, 30%). Recrystallization from MeOH afforded **20** as red crystals: mp 100–103 °C dec; IR (hexanes) ν_{CO} 2024, 1978, ν_{NO} 1752 cm^{-1}; ^{1}H NMR (CDCl$_3$, 20 °C) δ 8.0–7.1 (m, aromatic), 4.02 (s, CH$_2$Ph); ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C) δ 213.52, 213.48 (CO), 137.8 (aromatic), 136.9 (CH$_2$Ph), 134.0–123.8 (aromatic), 57.5, 56.8, 32.0 (C$_3$ ring). Complexes **22** were prepared as described in the following paper. Full characterization and spectroscopic data are described therein.[18]

Crystal and Molecular Structure Determination for Fe(η^3-C$_3$Ph$_2$-*t*-Bu)(CO)$_2$(NO) (15d). A red crystal selected for data collection was cemented to a fine glass fiber. Preliminary photographic characterization of the crystal revealed *mmm* Laue symmetry. Systematic absences in the diffraction data uniquely determined the orthorhombic space group *Pbca*. Least-squares refinement of the angular settings of 25 reflections (21° ≤ 2θ ≤ 28°) provided the unit-cell parameters given in Table I, which also contains details of data collection and structure refinement.

A learned-profile procedure was used to enhance the accuracy in the measurement of weak reflections; intensity data were corrected for *Lp* effects, but not for absorption (low μ; regular crystal shape; maximum/minumum transmission, 1.00/0.91).

Standard heavy-atom procedures provided the Fe atom location; subsequent difference Fourier syntheses located the remaining non-hydrogen atoms. A completely unambiguous resolution of

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(45) Johnson, A. W.; Kyllingstad, V. L. *J. Org. Chem.* **1966**, *31*, 334–336.

(46) Ross, D. R.; Waight, D. S. *J. Chem. Soc.* **1965**, 6710–6717.

(47) Compounds **22** were prepared from **15c** and **15d** as described in the following paper. Full spectroscopic data are also given therein.

(48) While satisfactory microanalysis results could not be obtained for this oxocyclobutenyl compound, tertiary phosphine derivatives have been fully characterized by microanalysis, as described in the following paper.[18]

the NO vs. CO positions was not possible, but for all structures with assigned NO and CO positions on iron atoms containing both ligands, the following relationships exist: $d(\text{Fe–N}) < d(\text{Fe–C})$ and $d(\text{N–O}) > d(\text{C–O})$.[44] These inequalities are consistent with the assignments we report and are additionally supported by the N(1), C(1), and C(2) thermal parameters which are more internally consistent than were the alternative assignments.

Final refinement by blocked-cascade techniques used a model with anisotropic thermal parameters for all non-hydrogen atoms, all hydrogen atoms were incorporated as fixed, but updated contributions with $d(\text{C–H}) = 0.96$ Å and a thermal parameter 1.2 times the isotropic equivalent for the C atom to which it was attached. The mean shift/esd maximum ratio for the last cycle was 0.065.

Atomic coordinates for the non-hydrogen atoms are given in Table II, and selected bond distances and angles are given in Table III. For additional crystallographic information see supplementary material.[29]

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Registry No. **8a**, 51509-08-1; **8b**, 100701-12-0; **8c**, 100701-14-2; **10a**, 69745-64-8; **10b**, 100701-11-9; **10c**, 100701-13-1; **12a**, 100701-15-3; **12b**, 100701-16-4; **12c**, 100701-17-5; **13a**, 82661-39-0; **13b**, 100813-53-4; **13c**, 100813-52-3; **13d**, 100813-51-2; **15a**, 82661-42-5; **15b**, 100701-18-6; **15c**, 100701-20-0; **15d**, 100701-22-2; **15e**, 100701-24-4; **18**, 100701-27-7; **19**, 100683-75-8; **20**, 100701-25-5; $[C_3Ph_3][BF_4]$, 741-16-2; $[C_3Ph_2H][BF_4]$, 26810-73-1; $[C_3Ph_2\text{-}t\text{-}Bu][BF_4]$, 100683-73-6; $CO_2(CO)_8$, 15226-74-1; $[PPN^+][Co(CO)_4]$, 53433-12-8; $[C_3\text{-}t\text{-}Bu_3][BF_4]$, 60391-90-4; $P(OPh)_3$, 101-02-0; PPh_3, 603-35-0; PMe_2Ph, 672-66-2; $[C_3Ph_3]Cl$, 58090-78-1; $Na[Fe(CO)_3NO]$, 25875-18-7; $[PPN][Fe(CO)_3NO]$, 61003-17-6; $[C_3Ph_2Me][BF_4]$, 65102-02-5; bis(triphenylcyclopentenyl) ether, 100701-26-6; phenylchlorodiazirine, 4460-46-2; phenylacetylene, 536-74-3; 3,3-dimethyl-1-phenyl-1-butyne, 4250-82-2; 1-(2-naphthyl)-3-phenyl-1-propene, 26227-05-4; 2-(bromoethyl)-naphthalene, 939-26-4; (2-naphthylmethyl)triphenylphosphonium bromide, 35160-95-3; phenylacetaldehyde, 122-78-1.

Supplementary Material Available: Tables of observed and calculated structure factors (Table 1S), bond lengths (Table 2S), bond angles (Table 3S), anisotropic temperature factors (Table 4S), and hydrogen coordinates and temperature factors (Table 5S) (13 pages). Ordering information is given on any current masthead page.

Reactions of (η^3-Cyclopropenyl)iron Complexes with Tertiary Phosphorus Ligands. Competition between Ligand Substitution and Cyclopropenyl Migration to Carbon Monoxide Followed by Ring Expansion To Give Oxocyclobutenyl Ligands

Russell P. Hughes,*[1] James M. J. Lambert, and John L. Hubbard

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

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Symmetrically substituted (oxocyclobutenyl)iron compound **7a** reacts with tertiary phosphorus ligands PR_2R' (R = R′ = OPh, OMe, Ph; R = Me, R′ = Ph) with substitution of one CO ligand to give compounds **8**, containing an asymmetric center at iron. Unsymmetrically substituted analogues **7b–d**, containing prochiral oxocyclobutenyl ligands, react with PPh_3 to give mixtures of diastereoisomers **9** and **10**. (η^3-Cyclopropenyl)iron complex **6a** likewise reacts with tertiary *phosphites* [$P(OR)_3$; R = Me, Ph] to give only the products **11a,b** of CO substitution but reacts with *phosphines* (PR_2Ph; R = Ph, Me) to give both the products **11d,e** of CO substitution and ring-expanded oxocyclobutenyl complexes **8c,d**. Unsymmetrically substituted cyclopropenyl complex **6c** reacts with PPh_3 to give CO substitution product **11f**, both diastereoisomeric oxocycylobutenyl complexes **9b** and **10b**, and the symmetrically substituted oxocyclobutenyl isomer **13a**. Cyclopropenyl complex **6b** yields no simple CO substitution product on reaction with PPh_3 but affords only ring-expanded products **9a**, **10a**, and **13b**. Cyclopropenyl complexes containing *tert*-butyl substituents, **6d,e**, give only CO substitution reactions with PPh_3, PMe_2Ph, and PMe_3. The mechanisms of these reactions are discussed. In particular it is shown that ligand-induced slippage of an unsymmetrically substituted cyclopropenyl ligand from η^3 to η^1 must generate a different η^1-cyclopropenyl isomer from that obtained by direct combination of $Fe(CO)_3NO^-$ anion and the identically substituted cyclopropenyl cation. Evidence is presented that (η^1-cyclopropenyl)iron complexes must be nonfluxional with respect to ring whizzing on a time scale comparable with their subsequent reactivity and that η^3 to η^1 slippage is suppressed by *tert*-butyl substituents on the cyclopropenyl ring.

Introduction

In the preceding paper we reported on the synthesis and characterization of some new η^3-cyclopropenyl and η^3-oxocyclobutenyl complexes of iron and cobalt.[2] In agreement with previously reported results of Kerber,[3] reaction of cyclopropenyl cations $[C_3Ph_2R]^+$ (R = Ph, *t*-Bu) with $Co_2(CO)_8$ afforded both cyclopropenyl complexes **1a,b** and oxocyclobutenyl complexes **2a,b**. In contrast, it was noted that virtually all cyclopropenyl cations reacted with the $Co(CO)_4^-$ anion to afford only oxocycylobutenyl complexes.[2,4] The lone exception involved the tri-*tert*-bu-

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(1) Alfred P. Sloan Research Fellow, 1980–1984.

(2) Hughes, R. P.; Lambert, J. M. J.; Whitman, D. W.; Hubbard, J. L.; Henry, W. P.; Rheingold, A. L., preceding paper in this issue.

(3) Chiang, T.; Kerber, R. C.; Kimball, S. D.; Lauher, J. W. *Inorg. Chem.* **1979**, *18*, 1687–1691.

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