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(Fe–N) < d(Fe–C) and d(N–O) > d(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(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]

Acknowledgment. R.P.H. is grateful to the National Science Foundation, to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Alfred P. Sloan Foundation, for generous support of this work. R.P.H. is also grateful for preprints from, and free and helpful discussions with, Professor R.R. Schrock (MIT) and Professor R.C. Kerber (SUNY Stony Brook). Dartmouth's Varian XL-300 NMR spectrometer and the University of Delaware diffractometer were purchased with funds from the National Science Foundation.

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; $[C_3Ph_2$-t-$Bu][BF_4]$, 100683-73-6; $CO_2(CO)_8$, 15226-74-1; $[PPN^+][Co(CO)_4]$, 53433-12-8; $[C_3$-t-$Bu_3][BF_4]$, 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

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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-

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

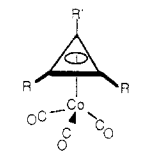
(2) Hughes, R. P.; Lambert, J. M. J.; Whitman, D. W.; Hubbard, J. L.; Henry, W. P.; Rheingold, A. L., preceding paper in this issue.

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

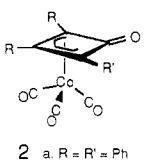
0276-7333/86/2305-0797$01.50/0

tylcyclopropenyl cation, which afforded both the cyclopropenyl complex **1c** and the oxocyclobutenyl complex **2c**.[2] Reaction of the cobalt cyclopropenyl complex **1a** with tertiary phosphine or phosphite ligands resulted in simple substitution of a CO ligand to give **3**, without any ring expansion to give the oxocyclobutenyl ligand.[2] In contrast, the reaction of the (triphenylcyclopropenyl)molybdenum complex **4a** with tertiary phosphorus ligands afforded only ring-expanded products **5a,b**. Curiously, the analogous (*tert*-butyldiphenylcyclopropenyl)molybdenum complex **4b** showed no reactivity toward exogenous ligands under thermal or photochemical conditions and gave no ring expansion or substitution of CO.[5]

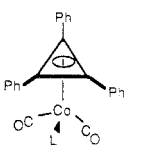
In contrast to $Co(CO)_4^-$, the isoelectronic anion $Fe(CO)_3(NO)^-$ was shown to react with cyclopropenyl cations to give both cyclopropenyl **6** and oxocyclobutenyl **7** complexes.[2] The most notable feature in both the cobalt and iron systems was that the oxocyclobutenyl complexes **2b** and **7b–d** formed from unsymmetrically substituted cyclpropenyl cations were exclusively those illustrated, in which the unique substituent (R′) occupied a site adjacent to the ketone function on the oxocyclobutenyl ring. No traces of the symmetrical isomers having R′ distal to the ketone function could be detected in NMR spectra of the crude reaction mixtures.



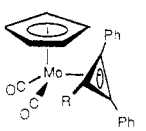
1 a. R = R′ = Ph
b. R = Ph; R′ = t-Bu
c. R = R′ = t-Bu



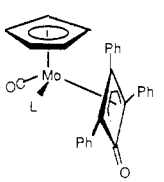
2 a. R = R′ = Ph
b. R = Ph; R′ = t-Bu
c. R = R′ = t-Bu



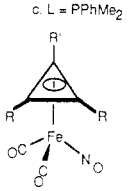
3 a. L = $P(OPh)_3$
b. L = PPh_3
c. L = $PPhMe_2$



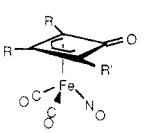
4 a. R = Ph
b. R = t-Bu



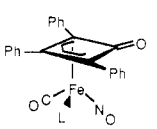
5 a. L = $P(OPh)_3$
b. L = $PPhMe_2$



6 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



7 a. R = R′ = Ph
b. R = Ph; R′ = H
c. R = Ph; R′ = Me
d. R = Ph; R′ = t-Bu

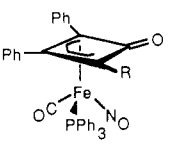


8 a. L = $P(OPh)_3$
b. L = $P(OMe)_3$
c. L = PPh_3
d. L = $PPhMe_2$

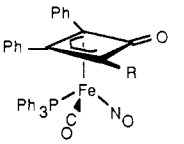
This paper describes a detailed study of the reactions of both cyclopropenyl- and (oxocyclobutenyl)iron complexes with tertiary phosphorus ligands.

Results

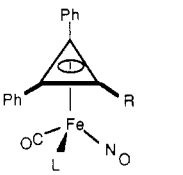
Reactions of (Oxocyclobutenyl)iron Complexes 7 with Tertiary Phosphines and Phosphites. In refluxing benzene, tertiary phosphites $P(OR)_3$ (R = Ph, Me) reacted with oxocyclobutenyl complex **7a** to give moderate to good yields of the substitution products **8a,b** as red, crystalline compounds, which were fully characterized spectroscopically and by elemental analysis. Similarly tertiary phosphines $PPhR_2$ (R = Ph, Me) reacted with **7a** to give the analogous complexes **8c,d**. The PMe_2Ph complex exhibited two diastereotopic phosphorus methyl resonances in its ^1H NMR spectrum, consistent with the presence of a configurationally stable (on the NMR time scale) asymmetric center at iron. The unsymmetrically substituted oxocyclobutenyl compounds **7b–d**, which contain a prochiral oxocyclobutenyl ring, likewise reacted with PPh_3 to give mixtures of diastereoisomers **9a–c** and **10a–c** (only one enantiomer of each diastereoisomeric pair is shown). No attempt was made to separate the diastereoisomers, but in each mixture two sets of resonances were observed for the R substituent in the ^1H and ^{13}C NMR spectra, two carbonyl carbon doublets due to coupling with phosphorus were observed in the ^{13}C NMR spectrum, and two ^{31}P NMR resonances were also observed. Integration of the two resonances for the R substituent in the ^1H NMR and the two ^{31}P resonances in the crude reaction mixtures were internally consistent and allowed a quantitative estimation of the ratio of diastereoisomers formed in this substitution reaction as 5:1 for **9a:10a**, 2:1 for **9b:10b**, and 2:1 for **9c:10c**.



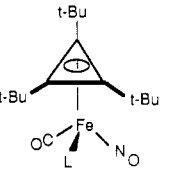
9 a. R = H
b. R = Me
c. R = t-Bu



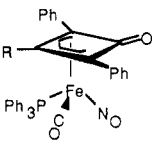
10 a. R = H
b. R = Me
c. R = t-Bu



11 a. R = Ph; L = $P(OPh)_3$
b. R = Ph; L = $P(OMe)_3$
c. R = t-Bu; L = PPh_3
d. R = Ph; L = PPh_3
e. R = Ph; L = $PPhMe_2$
f. R = Me; L = PPh_3



12 a. L = $PPhMe_2$
b. L = PMe_3



13 a. R = Me
b. R = H

These compounds served as important reference materials for further reactions described below.

Reactions of Cyclopropenyliron Complex 6a with Tertiary Phosphites. The cyclopropenyl complex **6a** also reacted with tertiary phosphites $P(OR)_3$ (R = Ph, Me) to afford good yields of the substitution products **11a,b** as red, crystalline compounds. IR monitoring of the reaction provided no evidence for formation of oxocyclobutenyl compounds. Observation that the three cyclopropenyl ring carbons in **11a,b** exhibit a single resonance in the ^{13}C NMR spectrum is consistent with fast rotation about the iron–C_3 axis on the NMR time scale and is consistent with results obtained for other cyclopropenyl compounds of Fe,[2] Co,[2] Mo,[5] and W.[5]

(4) Donaldson, W. A.; Hughes, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 4846–4859.
(5) Hughes, R. P.; Reisch, J. W.; Rheingold, A. L. *Organometallics* **1985**, *4*, 1754–1761.

Table I. Yields of C_3 and C_4 Products from Reactions of Cyclopropenyl Complexes with Exogenous Ligands L

starting material	cyclopropenyl ligand	L	% C_3	% C_4[a]
6a	C_3Ph_3	$P(OPh)_3$	85	0
6a	C_3Ph_3	$P(OMe)_3$	76	0
6a	C_3Ph_3	PPh_3	38	48
6a	C_3Ph_3	$PPhMe_2$	11	65
6b	C_3Ph_2H	PPh_3	0	42
6c	C_3Ph_2Me	PPh_3	12	58
6d	C_3Ph_2-*t*-Bu	PPh_3	67	0
6e	C_3-*t*-Bu_3	$PPhMe_2$	88	0
6e	C_3-*t*-Bu_3	PMe_3	72	0

[a] Overall yield of all isomers, where appropriate.

Reactions of Cyclopropenyliron Complexes 6b–e with Tertiary Phosphines. Cyclopropenyl complexes **6d** and **6e**, containing *tert*-butyl substituents on the three-membered ring, reacted with tertiary phosphines in refluxing benzene to afford only the product (**11c**, **12a,b**) of CO substitution. No spectroscopic evidence was obtained for formation of any oxocyclobutenyl complexes in these reactions. This is notable since the oxocyclobutenyl complex **9c** was prepared by reaction of **7d** with PPh_3 and is a stable compound. Observation of diastereotopic methyl resonances for the PMe_2Ph ligand in the ^1H NMR spectrum of **12a**, and two resonances for the phenylated carbon atoms in the C3 ring of **11c**, demonstrates the configurational stability of the asymmetric iron center in these compounds. The mechanistic possibility of epimerization at the metal via a metallacyclobutadiene intermediate is discussed in the preceding paper.[2]

In contrast the cyclopropenyl complex **6a** reacted smoothly with tertiary phosphines $PPhR_2$ (R = Ph, Me) to give high yields of mixtures of substitution products **11d,e** and the ring-expanded oxocyclobutenyl complexes **8c,d**, which were easily separable by column chromatography. Table I shows the yields of C3 and C4 products. The ^1H NMR spectrum of **11e** exhibited resonances for two diastereotopic phosphorus methyl groups, once again demonstrating the configurational stability of the asymmetric iron center. Oxocyclobutenyl complexes **8c,d** were spectroscopically identical with those formed by direct reaction of **7a** with the phosphine (vide supra).

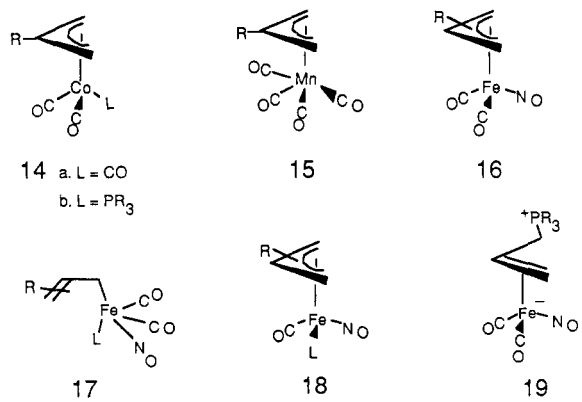
Further contrasting behavior was observed in the reactions of the unsymmetrically substituted cyclopropenyl complexes **6b,c** with triphenylphosphine. The methyl-substituted compound **6c** reacted with PPh_3 in toluene at 90 °C to give an overall 70% yield of a mixture of four complexes which were separated by preparative dry column chromatography. The cyclopropenyl product **11f** (12%) was characterized spectroscopically and by elemental analysis. The diastereoisomeric pair of compounds **9b** and **10b** (32% combined yield) was spectroscopically identical with that obtained by direct reaction of **7c** wth PPh_3 (vide supra), and the 2:1 ratio of diastereomers was identical with that produced in the latter reaction. The fourth product was unambiguously identified as the symmetrically substituted oxocyclobutenyl complex **13a** (26%). Since the oxocyclobutenyl ring in this compound is not prochiral, diastereoisomers are not possible. The IR spectrum of **13a** exhibited a single metal carbonyl band, a single metal nitrosyl stretch, and a typical oxocyclobutenyl ketone vibration. Its ^1H NMR spectrum showed a single methyl resonance, and the ^{13}C NMR spectrum displayed a single doublet resonance for the metal carbonyl carbon, four oxocyclobutenyl resonances, and a single methyl resonance, all at different chemical shifts from either of the diastereoisomers **9b** and **10b**. Therefore the only reasonable structure for **13a** is as shown, with the methyl group distal to the ketone function.

The cyclopropenyl complex **6b** also reacted smoothly with PPh_3 but afforded none of the product of simple CO substitution. Instead only the products of phosphine addition with ring expansion were obtained, albeit in relatively low yields. Diastereoisomeric products **9a** and **10a** (25% combined yield) were spectroscopically identical with those produced by direct reaction of **7b** with PPh_3, but in contrast to this latter reaction the ratio of diastereoisomers produced in the ring expansion reaction was 2:1 rather than 5:1 (vide supra). The symmetrically substituted oxocyclobutenyl complex **13b** (17%) was characterized completely by spectroscopic and microanalytical methods.

Discussion

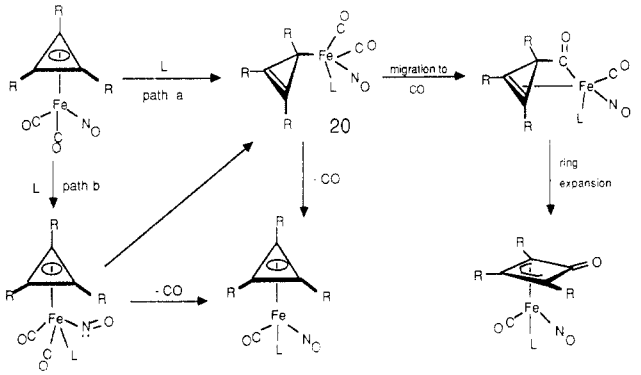
Reactions of (η^3-allyl)tricarbonylcobalt complexes **14a** with tertiary phosphines to yield the products (**14b**) of CO substitution have been shown to proceed via a dissociative mechanism.[6] A recent detailed study of the corresponding substitution reactions of (η^3-allyl)tetracarbonylmanganese complexes **15** indicates that these reactions also proceed via rate-determining loss of CO.[7] Substituents in the 2-position of the allyl ligand exert significant effects on the rate of CO dissociation, the rate decreasing as R = *t*-Bu > Ph > Me > H. Since the 2-substituent is known to eclipse one CO ligand, it has been suggested that steric acceleration of CO dissociation is an important effect in these reactions.[7]

In contrast, the η^3-allylic iron compounds **16** undergo CO substitution by an associative pathway.[8,9] When electronegative substituents, such as CN or halogens, were present on the allylic ligand, intermediate η^1-allyl complexes **17** could be isolated, but when methyl or phenyl substituents were present, no such intermediates could be detected spectroscopically, and only the η^3-allyl products **18** were isolated.[8] Two reaction pathways exist whereby the incoming phosphorus ligand could coordinate in an associative reaction. An η^3 to η^1 rearrangement of the allylic ligand would generate a vacant coordination site, or, alternatively a linear to bent rearrangement of the nitrosyl ligand could occur, followed either by subsequent η^3 to η^1 transformation of the allyl moiety or CO dissociation and conversion back to a linear metal–nitrosyl interaction. It is not clear why the former pathway should be facile for the iron systems, when it is clearly unimportant for the cobalt[6] and manganese[7] analogues, unless the NO ligand facilitates the η^3 to η^1 rearrangement in some way.

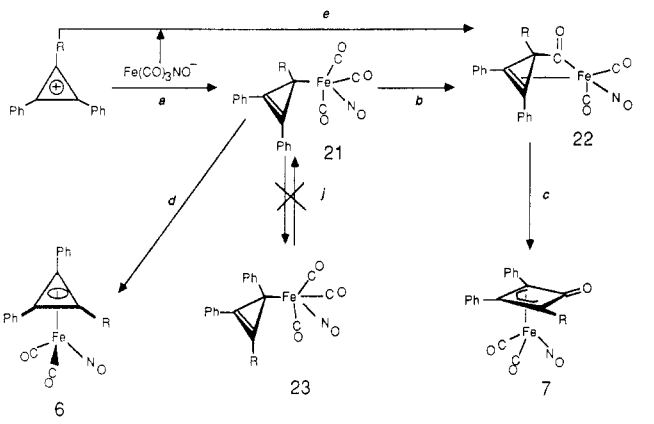


(6) Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 655–657.
(7) Palmer, G. T.; Basolo, F. *J. Am. Chem. Soc.* **1985**, *107*, 3122–3129.
(8) Cardaci, G.; Foffani, A. *J. Chem. Soc., Dalton Trans.* **1974**, 1808–1813.
(9) Cardaci, G. *J. Chem. Soc., Dalton Trans.* **1974**, 2452–2456.

Scheme I



Scheme II



Furthermore, with some substituted allyl ligands reactions with tertiary phosphites afforded products arising from allyl migration to CO in competition with CO substitution.[8] Use of basic phosphines (PR_3, R = Me, Et, *n*-Bu, Cy) and the parent allyl ligand led to products **19** resulting from nucleophilic addition of the phosphine to the allyl ligand.[10] Thus the initial step in these reactions is not always clearly defined or predictable, and subsequent chemistry is dependent both on the nature of the phosphorus donor and substituents on the allylic ligand.

Application of these possible pathways to a symmetrically substituted cyclopropenyl complex is summarized in Scheme I. By analogy with the acyclic allyl analogues discussed above, a key intermediate would seem to be **20**, although we cannot distinguish between the two possible associative pathways (a or b) by which this species can be approached. Intermediate **20** could then undergo one of two competitive reactions: loss of CO with concomitant η^1 to η^3 transformation of the cyclopropenyl ligand to give the product of simple ligand substitution or cyclopropenyl migration to CO followed by ring expansion to give the oxocyclobutenyl ligand. We have shown in previous studies that a (2-cyclopropene-1-carbonyl)metal species is a necessary precursor for formation of the ring-expanded oxocyclobutenyl ligand.[4]

Table I summarizes the product distributions obtained by using different cyclopropenyl precursors and different exogenous ligands. The yields given for C4 complexes represent the combined yields of all isomers, where appropriate.

Effect of the Phosphorus Ligand on Product Distribution. The nature of the exogenous ligand is clearly important in determining the rates at which the two divergent pathways proceed from the putative intermediate **20**, as evidenced by the observation that only CO substitution occurs when the ligand L is a tertiary phosphite but that mixtures of substitution product and ring-expanded product are formed when L is a phosphine. This effect is not simply a steric one since $P(OPh)_3$ and $P(OMe)_3$, phosphites with greatly differing cone angles, both give only substitution reactions with **6a**, whereas PPh_3 or $PPhMe_2$ afford competition between substitution and cyclopropenyl migration/ring expansion. A plausible rationale is that the rate of CO dissociation from intermediate **20** is enhanced (relative to phosphine analogues) by the stronger π-acceptor phosphite ligands, so that this pathway operates to the exclusion of cyclopropenyl migration. This is supported by the observation that the more basic phosphine $PPhMe_2$ gives relatively higher yields of oxocyclobutenyl product, perhaps by slowing the rate of CO dissociation, so that the rate of cyclopropenyl migration becomes more competitive. Unfortunately we have no means of assessing the relative effects of phosphine vs. phosphite on the rate of cyclopropenyl migration to CO. However it is curious that the results using acyclic allyliron compounds[8] (vide supra) indicate that allyl migration to CO occurs preferentially when using phosphite rather than phosphine ligands, in contrast to our observations.

Effect of Substituents on the Cyclopropenyl Ring. The substituents on the cyclopropenyl ring also have a profound effect on the product distribution. Although overall yields vary, our results clearly indicate that the presence of a *tert*-butyl group on the starting cyclopropenyl ring (**6d** or **6e**) suppresses ring expansion and affords only CO substitution, whereas the presence of a hydrogen atom at one of the ring sites (**6b**) leads to exclusive ring expansion. It is tempting to ascribe this difference to steric effects. The putative precursor to cyclopropenyl migration (**20**) would be crowded if one R group were *tert*-butyl and loss of CO should be accelerated in order to relieve steric congestion. Examination of the relative product distributions produced from reactions of **6a** and **6c** with PPh_3 supports this hypothesis, since the more sterically demanding cyclopropenyl ligand in **6a** gives significantly greater yields of C3 rather than C4 products (Table I). Alternatively the effect of cyclopropenyl ring substituents may be to affect the facility of η^3 to η^1 conversion of the cyclopropenyl ligand, with bulky groups slowing the rate of this reaction. Thus the entry of the exogenous ligand could be accommodated by a linear to bent transformation of the NO ligand, with subsequent chemistry controlled by the relative rates of loss of CO compared to formation of an η^1-cyclopropenyl intermediate. This latter explanation is in accord with the results obtained with cyclopropenylmolybdenum compounds, in which the triphenylcyclopropenyl system **4a** reacts with both phosphines and phosphites to give exclusive ring expansion, but the *tert*-butyl diphenyl analogue **4b** is completely unreactive toward both types of phosphorus ligand and does not undergo CO substitution.[5] This presumably reflects the suppression of an η^3 to η^1 rearrangement in the latter case since the flexible NO ligand is not available. Further evidence for this substituent effect is discussed below.

Similar effects on the relative facility of η^3 to η^1 conversions in η^3-allylic complexes of Pd(II) have been noted. Introduction of substituents R at the 2-position of the allyl ligand dramatically slows the rate of this dynamic process; *tert*-butyl is more effective than methyl.[11]

Mechanism of Formation of Oxocyclobutenyl Ligands. i. From Cyclopropenyl Cations. If we first

(10) Cardaci, G. *J. Chem. Soc., Dalton Trans.* **1984**, 815–818.

(11) Hughes, R. P.; Powell, J. *J. Organomet. Chem.* **1973**, *60*, 387 and references cited therein.

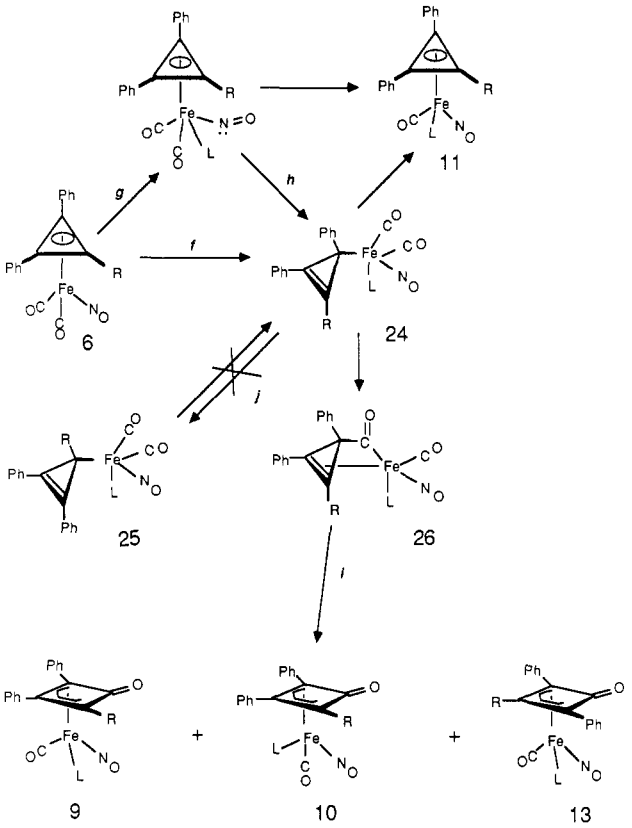
Table II. Yields of η^3-Cyclopropenyl Complexes 6 and Oxocyclobutenyl Complexes 7 from the Reaction of Cyclopropenyl Cations with the $Fe(CO)_3(NO)^-$ Anion[2]

cyclopropenyl cation	% C_3 (cyclopropenyl)	% C_4 (oxocyclobutenyl)	ratio C_3/C_4
C_3Ph_2H	6	52	0.11
C_3Ph_2Me	65	15	4.3
C_3Ph_3	36	52	0.69
C_3Ph_2-*t*-Bu	64	22	2.9
C_3-*t*-Bu_3	95	0	∞

consider the direct reaction of $Fe(CO)_3(NO)^-$ with an unsymmetrically substituted cyclopropenyl cation, the preferred site of nucleophilic attack on unsymmetrically substituted cyclopropenyl cations of this type is expected to be the non-phenylated position.[12,13] If such attack occurs at the iron center,[13] formation of the symmetrical (η^1-cyclopropenyl)metal intermediate **21** should occur, as shown in Scheme II (path a). Subsequent migration to CO via a 1,2 shift of the cyclopropenyl group[17] can yield only the symmetrical acyl complex **22** (path b), which in turn can only give rise to the unsymmetrical oxocyclobutenyl complex **7** by cleavage of one of the two equivalent C–C bonds of the cyclopropene ring (path c). When R is H, Me, Ph, or *t*-Bu, the reaction gives both the η^3-cyclopropenyl complex **6** and the unsymmetrical (where applicable) oxocyclobutenyl complex **7**, indicating that loss of CO from intermediate **21** (path d) must be competitive with cyclopropenyl migration to give **22** (path b). The ratio of cyclopropenyl to oxocyclobutenyl product formed increases as R = Me > *t*-Bu > Ph > H (Table II). It is unclear how this substituent variation would affect the relative rates of CO loss and of cyclopropenyl migration. The tri-*tert*-butylcyclopropenyl cation gives only cyclopropenyl complex, possibly due to steric acceleration of CO loss coupled with steric hindrance of cyclopropenyl migration. It should be noted, however, that reaction of this latter cation with $Co(CO)_4^-$ anion gives approximately equal yields of cyclopropenyl and oxocyclobutenyl complexes, whereas all other cations react with this cobalt anion to give exclusive formation of oxocyclobutenyl compounds. Clearly the relative rates of the two reaction pathways depend on a number of factors, and the current evidence does not allow clear distinctions to be made between them.

At first examination our results do not appear to allow for exclusion of the possibility that the two reaction products arise from different intermediates rather than from the common precursor **21**. Thus oxocyclobutenyl products may be obtained via direct attack of the cyclopropenyl cation at a CO ligand, to give **22** and thence **7** (paths e, c), and cyclopropenyl compounds **6** may be formed by competitive attack at iron to form **21**, which then loses CO (paths a, d). However, two observations make this option unlikely. First, results discussed below clearly demonstrate that oxocyclobutenyl ligands can be produced from η^3- and η^1-cyclopropenyl intermediates. Second, it would seem that attack at CO rather than at iron should be enhanced for cyclopropenyl ligands which are sterically demanding, but the most hindered cation C_3-*t*-Bu_3^+ gives only cyclopropenyl complex, which by this latter argument would arise from attack at iron. *For this system*, therefore, we argue that the most plausible conclusion is to assume the common intermediacy of **21**.[14]

Scheme III



ii. From η^3-Cyclopropenyl Ligand Precursors. The single most interesting observation encountered in this study is that exogenous ligand-induced ring expansion of unsymmetrically substituted η^3-cyclopropenyl ligands results in formation of significant amounts of the symmetrically substituted oxocyclobutenyl ligand as well as the unsymmetrically substituted isomer. Notably only the latter are produced in direct reactions of a variety of carbonylate anions of Cr,[19] Mo,[19] W,[19] Co,[2,4] and Fe[2] with unsymmetrically substituted cyclopropenyl cations. Scheme III is an extension of the general mechanism outlined in Scheme I. Both approaches to the η^1-cyclopropenyl intermediate (paths f and g, h) are shown, but it does not matter which of these routes is followed to this point. However, two possible η^1-cyclopropenyl intermediates, **25** and **24**, could be formed from the unsymmetrically substituted η^3-cyclopropenyl precursor. One of these, **25**, is isostructural with the intermediate **21** postulated in the direct reaction of the cyclopropenyl cation with $Fe(CO)_3NO^-$ and must therefore lead only to the unsym-

(12) (a) Breslow, R.; Hover, H.; Chang, H. W. *J. Am. Chem. Soc.* **1962**, *84*, 0000. (b) Padwa, A.; Blacklock, T. J.; Cordova, D. M.; Loza, R. *Ibid.* **1980**, *102*, 5648–5656.

(13) Gompper, R.; Bartmann, E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 456–457.

(14) We have established unequivocally that cyclopropenyl cations can react with other transition-metal carbonyl anions to give products resulting from attack at sites other than the metal center. Thus C_3-*t*-Bu_3^+ reacts with $M(\eta\text{-}C_5H_5)(CO)_3^-$ (M = Mo, W) by attack at the cyclopentadienyl ring[15] and with $Mo(\eta\text{-}C_5Me_5)(CO)_3^-$ by attack at a C–H bond of a methyl group.[16] Some circumstantial evidence that attack at CO may be possible has also been discussed elsewhere.[4,5,15]

(15) Green, M; Hughes, R. P. *J. Chem. Soc., Chem. Commun.* **1975**, 862.

(16) Grabowski, N. A.; Henry, W. P.; Hughes, R. P., unpublished observations.

(17) These mechanistic arguments all require that cyclopropenyl migration to CO occurs via a 1,2 shift, i.e., that the cyclopropenyl carbon atom originally bound to Fe becomes bound to carbon. In one case migration of a cyclopropenyl group from CO to Re has been shown to occur with allylic rearrangement of the cyclopropenyl group.[18]

(18) (a) Desrosiers, P. J.; Hughes, R. P. *J. Am. Chem. Soc.* **1981**, *103*, 5593. (b) DeSimone, D. M.; Desrosiers, P. J.; Hughes, R. P. *Ibid.* **1982**, *104*, 4842–4846.

(19) Hughes, R. P. *Kläui*, W.; Reisch, J. W.; Müller, A. *Organometallics* **1985**, *4*, 1761–1766.

metrical oxocyclobutenyl ligand as shown previously in Scheme II.

Of the two possible acyl precursors to the oxocyclobutenyl ligand only **26** can give rise to both the symmetrical and unsymmetrical isomers by cleavage of one or other of the inequivalent cyclopropene ring bonds (path i). Thus the (η^1-cyclopropenyl)- and (2-cyclopropene-1-carbonyl)iron intermediates formed by ligand-induced η^3 to η^1 rearrangement of **6** must be **24** and **26**, *different intermediates than those produced in the direct reaction of the cyclopropenyl cation with the iron anion* (vide supra, Scheme II).

Finally it must be noted that the pairs of η^1-cyclopropenyl intermediates **24** and **25** (Scheme III) and **21** and **23** (Scheme II) cannot equilibrate by migration of the metal around the three-membered ring (ring whizzing; path j) on a time scale competitive with the rate of cyclopropenyl migration to CO and subsequent ring expansion, or identical product distributions would be expected in both reactions. This latter point is consistent with our previous studies of (η^1-cyclopropenyl)rhenium complexes which demonstrated that such ring whizzing has a high free energy of activation (>32 kcal/mol) and is probably forbidden by orbital symmetry.[18]

We cannot exclude the possibility that η^3 to η^1 rearrangement of the cyclopropenyl ligand might lead to a nonequilibrating mixture of both intermediates **24** and **25**, but clearly **24** must be a major component of such a mixture.

Finally it is instructive to examine Schemes II and III while considering the products formed from *tert*-butyldiphenylcyclopropenyl precursors. Consideration of the arguments presented above indicates that the reaction of this cation with $Fe(CO)_3(NO)^-$ (Scheme II) presumably must proceed via η^1-cyclopropenyl intermediate **21** (R = *t*-Bu) in order to give both **6d** and only unsymmetrical **7d**. The reaction of η^3-cyclopropenyl precursor **6d** with triphenylphosphine gives only **11c** via loss of CO, with no formation of either symmetrical or unsymmetrical oxocyclobutenyl complexes. In view of our previous discussion it seems highly unlikely that this latter reaction proceeds via a η^1-cyclopropenyl intermediate, since this species should lead to at least some oxocyclobutenyl formation, as observed in the cyclopropenyl cation reaction. Clearly the two η^1-cyclopropenyl intermediates **21** (R = *t*-Bu) and **24** (R = *t*-Bu) are different; **21** (R = *t*-Bu) contains CO while **24** (R = *t*-Bu) would contain triphenylphosphine, and the cyclopropenyl ligands are bound to iron via different carbon atoms. However, our results using other cyclopropenyl ligands and a variety of ligands L indicate that there is no reason to suppose that **24** (R = *t*-Bu) should not undergo competitive loss of CO and cyclopropenyl migration/ring expansion.

We conclude that when an η^3-cyclopropenyl ligand has a *tert*-butyl substituent, η^3 to η^1 rearrangement is suppressed and that CO substitution occurs via an associative pathway with NO bending allowing initial coordination of th exogenous ligand. This may be the pathway by which all incoming ligands initially coordinate to iron (see Scheme I), and subsequent chemistry may be controlled simply by the relative efficacy of η^3 to η^1 rearrangement of the cyclopropenyl ligand compared to loss of CO.

Conclusions

We have shown that η^3-cyclopropenyl compounds of iron can serve as precursors for formation of oxocyclobutenyl complexes, provided that tertiary phosphines rather than phosphites are used as the exogenous ligands. It is also clear that any η^1-cyclopropenyl intermediates formed in these phosphine-induced reactions must be ligated to iron through a different carbon atom than are the putative η^1-cyclopropenyl intermediates generated in the direct reaction of cyclopropenyl cations with $Fe(CO)_3(NO)^-$ anion. Our results also demonstrate that η^1-cyclopropenyl iron complexes cannot undergo fast ring-whizzing reactions and that the efficacy of η^3 to η^1 rearrangement of η^3-cyclopropenyl ligands is strongly dependent on the ring substituents; in particular, the presence of one or more *tert*-butyl groups on the cyclopropenyl ring appears to suppress this rearrangement.

Experimental Section

General Comments. General conditions under which solvents were purified, experiments were conducted, and spectral and microanalytical results were obtained are described in the preceding paper.[2] Cyclopropenyl- and (oxocyclobutenyl)iron complexes were also prepared as previously described.[2]

Reaction of $Fe(\eta^3$-$C_3Ph_3CO)(CO)_2NO$ (7a) with Triphenyl Phosphite [$P(OPh)_3$]. A mixture of **7a** (2.21 g, 5.04 mmol) and $P(OPh)_3$ (1.64 g, 5.30 mmol) in dry, deoxygenated benzene (30 mL) was refluxed (4 h). The solvent was removed in vacuo, and the residue was chromatographed on a Florisil/hexanes column (20 × 300 mm). Hexanes/Et_2O (1:1) eluted a red band which, after removal of solvent, yielded a red glassy solid identified as $Fe(\eta^3$-$C_3Ph_3CO)(CO)(NO)(P(OPh)_3)$ (**8a**; 1.21 g, 1.68 mmol, 33%). This material was recrystallized from warm acetonitrile (50 °C) to give **8a** as orange needles: mp 85 °C (darkens, softens), 100 °C dec; IR (CH_2Cl_2): ν_{CO} 2015, ν_{NO} 1780, $\nu_{C=O}$ 1702 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 7.9–6.6 (m, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 215.0 (d, CO, J_{PC} = 13 Hz), 164.6 (d, C=O, J_{PC} = 2 Hz), 150.6 (d, ipso-Ph, J_{PC} = 10 Hz), 133.7–120.9 (14 lines, Ph), 95.8 (*C*Ph), 93.1 (*C*Ph); MS (FAB), *m/e* 720 (P^+), 692 (P^+ – CO), 633 (P^+ – 2CO), 633 (P^+ – 2CO – NO), 324 (P^+ – 2CO – NO – $P(OPh)_3$), 267 ($C_3Ph_3^+$). Anal. Calcd for $C_{41}H_{30}FeNO_6P$: C, 68.44; H, 4.20; N, 1.95. Found: C, 68.65; H, 4.29; N, 1.91.

Reaction of $(\eta^3$-$C_3Ph_3CO)Fe(CO)_2NO$ (7a) with Trimethyl Phosphite [$P(OMe)_3$]. A mixture of **7a** (1.45 g, 3.32 mmol) and $P(OMe)_3$ (0.41 mL, 3.5 mmol) in dry, deoxygenated benzene (30 mL) was refluxed (3.5 h). The solvent was removed, and the residue was chromatographed on a Florisil/hexanes column (19 × 310 mm). Et_2O eluted a red band which, after removal of solvent, yielded a red solid identified as spectroscopically pure $Fe(\eta^3$-$C_3Ph_3CO)Fe(CO)(NO)(P(OMe)_3)$ (**8b**; 1.43 g, 2.68 mmol, 81%). Crystallization from CH_2Cl_2/hexanes yielded analytically pure orange crystals: mp 56–59 °C; IR (CH_2Cl_2) ν_{CO} 1995, ν_{NO} 1765, $\nu_{C=O}$ 1685 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 8.3–6.5 (m, Ph, 15 H), 3.44 (d, Me, 9 H, J_{PH} = 12 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 216.7 (d, CO, J_{PC} = 20 Hz), 165.0 (C=O), 135.9–127.5 (9 lines, Ph), 97.2 (*C*Ph), 91.1 (d, *C*Ph, J_{PC} = 2 Hz), 52.0 (br, CH_3). Anal. Calcd for $C_{26}H_{24}FeNO_5P$: C, 58.56; H, 4.54; N, 2.63. Found: C, 58.88; H, 4.78; N, 2.75.

Reaction of $Fe(\eta^3$-$C_3Ph_3CO)(CO)_2NO$ (7a) with Triphenylphosphine (PPh_3). A mixture of **7a** (0.500 g, 1.14 mmol) and PPh_3 (0.330 g, 1.26 mmol) in dry deoxygenated benzene (15 mL) was refluxed (10 h). The solvent was removed in vacuo, and the residue was chromatographed on a Florisil/CH_2Cl_2 column (23 × 300 mm). Et_2O eluted an orange band which, after evaporation of solvent, yielded a red solid identified as $Fe(\eta^3$-$C_3Ph_3CO)(CO)(NO)(PPh_3)$ (**8c**; 0.547 g, 0.815 mmol, 71%). Recrystallization from warm (50 °C) MeOH afforded **8c** as red-black crystals: mp 149 °C dec; IR (CH_2Cl_2) ν_{CO} 1990, ν_{NO} 1752, $\nu_{C=O}$ 1677 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 7.7–6.8 (m, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 219.6 (d, CO, J_{PC} = 6 Hz), 164.6 (d, C=O, J_{PC} = 7 Hz), 134.1–127.2 (24 lines, Ph), 94.8, 91.2, 86.7 (*C*Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 48.48; MS (FAB), *m/e* 672 (P^+), 644 (P^+ – CO), 615 (P^+ – CO, NO), 267 ($C_3Ph_3^+$). Anal. Calcd for $C_{41}H_{30}FeNO_3P$: C, 73.33; H, 4.50; N, 2.09. Found: C, 73.40; H, 4.57; N, 2.10.

Reaction of $(\eta^3$-$C_3Ph_3CO)Fe(CO)_2NO$ (7a) with Dimethylphenylphosphine (PMe_2Ph). A mixture of **7a** (0.35 g, 0.83 mmol) and PMe_2Ph (0.12 mL, 0.87 mmol) in dry, deoxygenated benzene (20 mL) was refluxed (7 h). The solvent was

removed in vacuo, and the residue was chromatographed on a Florisil/CH_2Cl_2 column (19 × 230 mm). Et_2O eluted an orange band which, after evaporation of solvent, yielded an air-sensitive orange oil identified as Fe(η^3-C_3Ph_3CO)(CO)(NO)(PMe_2Ph) (**8d**; 0.390 g, 0.71 mmol, 86%). Attempts to recrystallize this material resulted in decomposition: IR (CH_2Cl_2) ν_{CO} 1988, ν_{NO} 1749, $\nu_{C=O}$ 1648 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 8.2–6.3 (m, aromatic), 1.27 (d, PMe, J_{PH} = 5 Hz), 1.13 (d, PMe, J_{PH} = 7 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 167.5 (C=O), 140.5, 140.2, 138.0, 137.0, 136.7, 127.7 (br, Ph), 82.5 (*C*Ph), 68.0 (*C*Ph), 13.3 (br, PCH_3) (metal carbonyl resonance not observed).

Reaction of (η^3-C_3Ph_2HCO)$Fe(CO)_2NO$ (7b) with Triphenylphosphine (PPh_3). A mixture of **7b** (0.430 g, 1.19 mmol) and PPh_3 (0.328 g, 1.25 mmol) in dry, deoxygenated benzene (50 mL) was refluxed 10 h. The solvent was removed in vacuo, and the residue was chromatographed on a Florisil/hexanes column (21 × 170 mm). Et_2O first eluted unreacted **7b** (0.019 g, 0.053 mmol, 12%) followed by an orange band which, after removal of solvent, afforded an orange-red powder identified as a mixture of the diastereoisomers Fe(η^3-C_3Ph_2HCO)(CO)(NO)(PPh_3) (**9a/10a**; 0.547 g, 0.919 mmol, 77%). Recrystallization from MeOH (−25 °C) afforded red cubes, mp 158–160 °C dec. To ensure accurate characterization of the ratio of both diastereoisomers, the IR and NMR spectra were taken of the unrecrystallized material: IR (CH_2Cl_2) ν_{CO} 1989, ν_{NO} 1757, $\nu_{C=O}$ 1688 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 7.9–6.7 (m, Ph, 25 H), 4.71 (d, H, J_{PH} = 9 Hz), 4.27 (d, H, J_{PH} = 9 Hz) total area for both protons = 1 H; relative intensity of δ 4.71/δ 4.27 = 5:1); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 218.2 (d, $^2J_{PC}$ = 12 Hz, major), 215.2 (d, $^2J_{PH}$ = 12 Hz, minor) (CO), 166.1 (major), 165.7 (minor) (C=O), 133.8–127.3 (14 lines, Ph), 98.7 (major), 97.2 (minor) (*C*Ph), 86.1 (minor), 84.5 (major) (*C*Ph), 74.6 (major) 71.7 (minor) (CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 66.06 (minor), 59.91 (major); MS (FAB), *m/e* 596 (P^+), 568 (P^+ − CO), 538 (P^+ − CO − NO). Anal. Calcd for $C_{35}H_{26}FeNO_3P$: C, 70.60; H, 4.40; N, 2.45. Found: C, 70.33; H, 4.49; N, 2.26.

Reaction of Fe(η^3-C_3Ph_2MeCO)$(CO)_2NO$ (7c) with Triphenylphosphine (PPh_3). A mixture of **7c** (0.240 g, 0.640 mmol) and PPh_3 (0.185 g, 0.704 mmol, 10% excess) in dry, deoxygenated benzene (25 mL) was warmed in a 65 °C oil bath (12 h). The solvent was removed in vacuo, and the residue was chromatographed on a Florisil/CH_2Cl_2 column (22 × 210 mm). CH_2Cl_2 eluted a red band which, after removal of solvent, afforded a red solid identified as a mixture of the diastereoisomers Fe(η^3-C_3Ph_2MeCO)(CO)(NO)(PPh_3) (**9b/10b**; 0.144 g, 0.236 g, 37%): IR (CH_2Cl_2) ν_{CO} 1984, ν_{NO} 1747, $\nu_{C=O}$ 1678 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 7.8–7.0 (m, Ph, 25 H), 1.89 (d, Me, J_{PH} = 4 Hz), 1.66 (d, Me, J_{PH} = 3 Hz) (ratio of aromatic/methyl protons = 25:3; relative area of δ 1.89/δ 1.66 = 1:2); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 219.3 (d, $^2J_{PC}$ = 9 Hz, major), 219.2 (d, $^2J_{PC}$ = 10 Hz, minor) (CO), 167.6 (br, minor), 167.3 (d, $^2J_{PC}$ = 2 Hz, major) (C=O), 134.1–127.1 (15 lines, Ph), 96.5 (major), 96.4 (minor) (*C*Ph), 90.3 (major), 89.8 (minor) (*C*Ph), 85.5 (minor), 84.4 (major) (*C*Me), 10.6 (major), 10.3 (minor) (CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 55.00 (major), 53.60 (minor). The crude material was recrystallized from MeOH to yield red cubes: MS (FAB), *m/e* 610 (P^+), 582 (P^+ − CO), 552 (P^+ − CO − NO). Anal. Calcd for $C_{36}H_{28}FeNO_3P$: C, 70.95; H, 4.63; N, 2.30. Found: C, 70.42, H, 5.03; N, 2.18.

Reaction of Fe(η^3-C_3Ph_2-*t*-BuCO)$(CO)_2NO$ (7d) with Triphenylphosphine (PPh_3). A mixture of **7d** (0.343 g, 0.822 mmol) and PPh_3 (0.237 g, 0.904 mmol) in dry, deoxygenated benzene (20 mL) was warmed in a 65 °C oil bath (12 h). The solvent was removed in vacuo, and the residue was chromatographed on a Florisil/CH_2Cl_2 column (22 × 200 mm). CH_2Cl_2 eluted an orange band identified by IR as starting material (**7d**) (0.050 g, 0.120 mmol, 15%). Et_2O then eluted a red band which, after removal of solvent, yielded a red oil identified as a mixture of the diastereomers Fe(η^3-C_3Ph_2-*t*-BuCO)(CO)(NO)(PPh_3) (**9c/10c**; 0.335 g, 0.514 mmol, 63%): IR (CH_2Cl_2) ν_{CO} 1972, ν_{NO} 1740, $\nu_{C=O}$ 1674 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 7.8–6.6 (m, Ph, 25 H), 1.36, 1.32 (s, *t*-Bu, 9 H) (relative intensities of peaks at δ 1.36/δ 1.32 = 2:1); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 221.6 (d, $^2J_{PC}$ = 12 Hz, major), 217.3 (d, $^2J_{PC}$ = 11 Hz, minor) (CO), 167.3 (minor), 166.9 (major) (C=O), 135.7–125.7 (9 lines, Ph), 100.1 (d, J_{PC} = 13 Hz, major), 100.0 (d, J_{PC} = 13 Hz, minor) (CPh), 97.0 (minor), 92.1 (major) (CPh), 62.3 (minor), 61.0 (major) (*C*-*t*-Bu), 34.7 (minor), 34.5 (major) (*C*Me_3), 29.4 (br, CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 58.99 (minor), 52.26 (major). All attempts to recrystallize the red oil failed to give analytically pure material.

Reaction of Fe(η^3-C_3Ph_3)$(CO)_2NO$ (6a) with Triphenyl Phosphite [$P(OPh)_3$]. A solution of **6a** (0.500 g, 1.22 mmol) and $P(OPh)_3$ (0.35 mL, 1.3 mmol) in dry, deoxygenated benzene (20 mL) was refluxed for 8 h. The solvent was removed, and the residue was chromatographed on a Florisil/hexanes column (20 × 300 mm). Elution with hexanes/Et_2O (4:1) removed a red band which, after removal of solvent, yielded a red solid identified as Fe(η^3-C_3Ph_3)(CO)(NO)($P(OPh)_3$) (**11a**; 0.72 g, 1.04 mmol, 85%): IR (CH_2Cl_2) ν_{CO} 1981, ν_{NO} 1731 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 7.9–6.6 (m, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 216.3 (CO), 151.1 (d, POC, $^2J_{PC}$ = 7 Hz), 133.6 (sh, Ph), 129.4, 124.5, 121.0 (br, Ph), 51.5 (d, *C*Ph, J_{PC} = 3 Hz). This material was recrystallized from CH_2Cl_2/hexanes to afford red cubes: mp 158–159 °C. Anal. Calcd for $C_{40}H_{30}FeNO_5P$: C, 69.48; H, 4.37; N, 2.03. Found: C, 69.39; H, 4.22; N, 2.08.

Reaction of Fe(η^3-C_3Ph_3)$(CO)_2NO$ (6a) with Trimethyl Phosphite [$P(OMe)_3$]. A solution of **6a** (0.500 g, 1.22 mmol) and $P(OMe)_3$ (0.16 mL, 1.3 mmol) in dry, deoxygenated benzene (20 mL) was refluxed (16 h). The solvent was removed leaving a red oil which was chromatographed on a Florisil/hexanes column (15 × 200 mm). Elution with hexane/Et_2O (9:1) removed a red band which, after removal of solvent, yielded a red solid identified as Fe(η^3-C_3Ph_3)(CO)(NO)($P(OMe)_3$) (**11b**; 0.47 g, 0.93 mmol, 76%). Recrystallization from hexane afforded red cubes: mp 79–80 °C; IR (CH_2Cl_2) ν_{CO} 1972, ν_{NO} 1724 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.3–6.5 (m, Ph, 15 H), 3.30 (d, Me, 9 H, J_{PH} = 12 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 219.6 (d, CO, J_{PC} = 5 Hz), 134.0 (sh, Ph), 129.4, 128.3 (br, Ph), 51.4 (d, *C*Ph, J_{PC} = 2 Hz). Anal. Calcd for $C_{25}H_{24}FeNO_5P$: C, 59.43; H, 4.79; N, 2.77. Found: C, 59.32; H, 4.78; N, 2.82.

Reaction of Fe(η^3-C_3Ph_3)$(CO)_2NO$ (6a) with Triphenylphosphine (PPh_3). A mixture of **6a** (0.500 g, 1.22 mmol) and PPh_3 (0.336 g, 1.28 mmol) in dry, deoxygenated benzene (25 mL) was refluxed (10 h). The solvent was removed, and the resiude was chromatographed on a Florisil/hexanes column (22 × 300 mm). Hexane/CH_2Cl_2 (1:1) eluted a red band which, after removal of solvents, yielded a red solid identified as Fe(η^3-C_3Ph_3)(CO)(NO)(PPh_3) (**11d**; 0.303 g, 0.467 mmol, 38%). Recrystallization from warm, dry MeOH afforded red needles: mp 132–134 °C dec; IR (CH_2Cl_2) ν_{CO} 1951, ν_{NO} 1709 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 7.5–6.9 (m, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 221.1 (d, CO, J_{PC} = 2 Hz), 135.3, 134.5, 133.6, 132.9, 129.4, 128.2, 127.5, 126.6 (Ph), 51.8 (d, *C*Ph, J_{PC} = 2 Hz); MS (FAB) *m/e* 644 (P^+), 615 (P^+ − CO), 585 (P^+ − CO − NO), 267 ($C_3Ph_3^+$). Anal. Calcd for $C_{40}H_{30}FeNO_2P$: C, 74.66; H, 4.70; N, 2.18. Found: C, 74.74; H, 7.73; N, 2.16. Et_2O eluted a second red band which, after removal of solvent, yielded a red solid identified as Fe(η^3-C_3Ph_3CO)(CO)(NO)(PPh_3) (**8c**; 0.396 g, 0.590 mmol, 48%). This material was identified spectroscopically by comparison to the same compound synthesized from **7a** and PPh_3 (vide supra).

Reaction of Fe(η^3-C_3Ph_3)$(CO)_2NO$ (6a) with Dimethylphenylphosphine (PMe_2Ph). A mixture of **6a** (0.585 g, 1.43 mmol) and PMe_2Ph (0.20 mL, 1.5 mmol) in dry, deoxygenated benzene (25 mL) was refluxed (10 h). The solvent was removed in vacuo and the residue was chromatographed on a Florisil/hexanes column (22 × 270 mm). Hexanes/CH_2Cl_2 (1:1) eluted a red band which, after removal of solvent, yielded an air-sensitive orange solid identified as Fe(η^3-C_3Ph_3)(CO)(NO)(PMe_2Ph) (**11e**; 0.080 g, 0.15 mmol, 11%): IR (hexane) ν_{CO} 1960, ν_{NO} 1719 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 6.8–7.5 (m, Ph, 20 H), 1.48 (d, PMe, 3 H, J_{PH} = 8 Hz), 1.34 (d, PMe, 3 H, J_{PH} = 8 Hz). Attempts to recrystallize **11e** led only to decomposition. Elution with Et_2O afforded Fe(η^3-C_3Ph_3CO)(CO)(NO)(PMe_2Ph) (**8d**) as an air-sensitive orange oil (0.51 g, 0.93 mmol, 65%) identified by IR and NMR: IR (hexane) ν_{CO} 1992, ν_{NO} 1754, $\nu_{C=O}$ 1679 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 8.2–6.3 (m, Ph, 20 H), 1.24 (d, PMe, 3 H, J_{PH} = 8 H), 1.15 (d, PMe, 3 H, J_{PH} = 8 Hz). This material also suffered extensive decomposition in all attempts to recrystallize it.

Reaction of Fe(η^3-C_3Ph_2Me)$(CO)_2NO$ (6c) with Triphenylphosphine (PPh_3). A mixture of **6c** (1.02 g, 2.93 mmol) and PPh_3 (0.845 g, 3.22 mmol) in dry, deoxygenated toluene (40 mL) was warmed for 12 h in a 90 °C oil bath. The IR spectrum indicated that the starting material had been consumed and TLC showed the presence of four compounds in the reaction mixture.

The solvent was removed in vacuo, and the residue (2.0 g) was chromatographed on a silica gel dry column (1 × 50 in) (Woelm silica, TSC, activity III) using CH_2Cl_2 as eluent. Four colored bands were separated by slicing them out of the column and removing the material from the silica with ethyl acetate. TLC of the material in the first band (R_f 1.0) showed the presence of more than a single compound so the material was rechromatographed on a medium-pressure liquid chromatograph (Silica gel packing (15 × 210 mm), 80–120 psi solvent pressure) packed with hexanes. The IR spectrum of the first material eluted with hexanes showed no carbonyl or nitrosyl peaks of interest. Hexanes/CH_2Cl_2 (1:1) eluted a second, red band off the column which was isolated as a red solid identified as Fe(η^3-C_3Ph_3Me)(CO)(NO)(PPh_3) (**11f**; 0.211 g, 0.363 mmol, 12%). Recrystallization from CH_2Cl_2/hexanes afforded **11f** as red cubes (0.171 g, 0.294 mmol, 10%): mp 148–150 °C dec; IR (CH_2Cl_2) ν_{CO} 1952, ν_{NO} 1705 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 7.6–7.1 (m, Ph, 25 H), 1.90 (d, Me, 3 H, J_{PH} = 2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 221.9 (CO), 135.7–126.4 (15 lines, Ph), 53.2 (*C*Ph), 51.1 (*C*Ph), 49.4 (d, *C*Me, J_{PC} = 4 Hz), 9.3 (CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 54.96; MS (FAB) *m/e* 582 (P^+), 553 (P^+ – CO), 523 (P^+ – CO – NO), 205 ($C_3Ph_2Me^+$). Anal. Calcd for $C_{35}H_{28}FeNO_2P$: C, 72.30; H, 4.85; N, 2.41. Found: C, 72.28, H, 5.01; N, 2.27. The second band (R_f 0.70) from the dry column was identified as unreacted starting material (**6c**) by its IR spectrum and was recovered (0.014 g, 0.04 mmol, 1%). The third band (R_f 0.25) was identified as the symmetrical oxocyclobutenyl complex **13a** and was isolated as red crystals (0.468 g, 0.768 mmol, 26%) which were only slightly soluble in CH_2Cl_2. The compund was recrystallized from CH_2Cl_2/hexanes as red needles: IR (CH_2Cl_2) ν_{CO} 1966, ν_{NO} 1740, $\nu_{C=O}$ 1678 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 7.9–6.9 (m, Ph, 25 H), 2.18 (s, Me, 3 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 218.9 (d, CO, J_{PC} = 12 Hz), 164.8 (C=O), 135.3–126.5 (15 lines, Ph), 95.1 (*C*Ph), 92.4 (*C*Ph), 82.8 (d, *C*Me, J_{PC} = 6 Hz), 13.3 (CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 55.35; MS (FAB), *m/e* 610 (P^+), 582 (P^+ – CO), 552 (P^+ – CO – NO), 290 (P^+ – CO – NO – PPh_3), 262 (PPh_3^+). Anal. Calcd for $C_{36}H_{28}FeNO_3P$: C, 70.95; H, 4.63; N, 2.30. Found: C, 70.83; H, 4.72; N, 2.22. The fourth band (R_f 0.10) was isolated as a red glassy solid identified as a diastereoisomeric mixture of the unsymmetrical oxocyclobutenyl complexes **9b/10b** (0.562 g, 0.922 mmol, 32%). These were the same compounds as those synthesized by reaction of **7c** with PPh_3 (vide supra) by comparison of spectroscopic data. The ratio of diastereomers was the same as in the direct substitution reaction as determined from the ^1H NMR spectrum.

Reaction of Fe(η^3-C_3Ph_2H)$(CO)_2NO$ (6b) with Triphenylphosphine (PPh_3). A mixture of **6b** (0.250 g, 0.750 mmol) and PPh_3 (0.206 g, 0.788 mmol) in dry, deoxygenated benzene (10 mL) was refluxed gently for 2 h. The solvent was removed in vacuo, and the residue was chromatographed on a silica gel dry column (1 × 40 in.) as above with $CHCl_3$ as eluent. Two bands separated, the column was sliced up, and the material was washed from the silica using ethyl acetate. The first band (R_f 0.18) was identified as the symmetrical oxocyclobutenyl complex **13b** and was isolated as an orange solid (0.07 g, 0.131 mmol, 17%): IR (CH_2Cl_2) ν_{CO} 1996, ν_{NO} 1760, $\nu_{C=O}$ 1685 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 7.7–6.8 (m, Ph, 25 H), 5.05 (s, CH, 1 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 218.4 (d, CO, J_{PC} = 11 Hz), 164.5 (C=O), 134.7–126.6 (17 lines, Ph), 90.0 (*C*Ph), 74.5 (CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 75.75. Recrystallization from CH_2Cl_2/hexanes afforded **13b** as an orange powder, mp 177 °C dec. Anal. Calcd for $C_{35}H_{26}FeNO_3$: C, 70.60; H, 4.40; N, 2.35. Found: C, 70.73; H, 4.46; N, 2.25. The second band was identified as a diastereoisomeric mixture of the unsymmetrical oxocyclobutenyl complexes **9a/10a** by comparison of spectral data to **9a/10a** prepared by the direct substitution route. The mixture **9a/10a** was obtained as a red solid (0.112 g, 0.188 mmol, 25%) and was recrystallized from MeOH to afford red cubes. The ratio of diastereomers from this reaction (before recrystallization) was determined to be 2:1 based on relative intensities of ^1H NMR resonances at δ 4.71/δ 4.26.

Reaction of Fe(η^3-C_3Ph_2-*t*-Bu)$(CO)_2NO$ (6d) with Triphenylphosphine (PPh_3). A mixture of **6d** (1.16 g, 2.99 mmol) and PPh_3 (0.862 g, 3.28 mmol) in dry, deoxygenated toluene (30 mL) was warmed to 90 °C (32 h). The solvent was removed in vacuo, leaving a red solid (1.9 g) which was chromatographed on a silica/hexanes column (22 × 250 mm). CH_2Cl_2 eluted a red band which, after removal of solvent, yielded a red solid identified as Fe(η^3-C_3Ph_2-*t*-Bu)(CO)(NO)(PPh_3) (**11c**; 1.25 g, 2.00 mmol, 67%). Recrystallization of this material from CH_2Cl_2/hexanes (−25 °C) afforded red needles: mp 142–145 °C dec; IR (CH_2Cl_2) ν_{CO} 1953, ν_{NO} 1718 cm^{-1}; ^1H NMR ($CDCl_3$, 20 °C) δ 7.5–6.9 (m, Ph, 25 H), 1.35 (s, CMe_3, 9 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 222.5 (d, CO, J_{PC} = 1 Hz), 136.0–126.0 (17 lines, Ph), 62.0 (d, *C*Ph, J_{PC} = 9 Hz), 61.7 (d, *C*Ph, J_{PC} = 2 Hz), 47.8 (*C*-*t*-Bu), 33.6 (*C*Me_3), 30.3 (CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 53.16; MS (FAB), *m/e* 624 (P^+), 595 (P^+ – CO), 565 (P^+ – CO – NO), 247 (C_3Ph_2-*t*-Bu^+). Anal. Calcd for $C_{38}H_{34}FeNO_2P$: C, 73.80; H, 5.49; N, 2.26. Found: C, 73.84; H. 5.55; N, 2.21. Subsequent elution with more polar solvents did not remove any material exhibiting metal carbonyl or nitrosyl bands in the IR spectrum.

Reaction of Fe(η^3-C_3-*t*-Bu_3)$(CO)_2NO$ (6e) with PMe_2Ph. A solution of **6e** (0.12 g, 0.27 mmol) and PMe_2Ph (0.050 g, 0.36 mmol) in benzene (20 mL) was refluxed for 43 h and then cooled. The solution was filtered through a 1 in. × 2 in. Florisil column, and the column was washed with benzene. The filtrate was evaporated to dryness, and the residue was recrystallized from hexane, to give the product Fe(η^3-C_3-*t*-Bu_3)(CO)(NO)(PMe_2Ph) (**12a**) as orange red prisms (0.14 g, 88%): mp 124–125 °C; IR (hexanes) ν_{CO} 1940, ν_{NO} 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3–7.6 (m, 5 H, Ph), 1.80 (d, J_{PH} = 7 Hz, 3 H, PMe), 1.75 (d, J_{PH} = 7 Hz, 3 H, PMe), 1.15 (s, 27 H, *t*-Bu); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 225.5 (CO), 144.8, 142.4, 129.3, 129.2, 128.3, 128.1 (Ph), 72.14 (*C*-*t*-Bu), 31.9 (*C*Me_3), 31.7 (C*Me*$_3$), 19.8 (d, J_{PC} = 22 Hz, P*Me*), 18.9 (d, J_{PC} = 22 Hz, P*Me*). Anal. Calcd for $C_{24}H_{38}FeNO_2P$: C, 62.75; H, 8.34; N, 3.05. Found: C, 62.62; H, 8.40; N, 2.91.

Reaction of Fe(η^3-C_3-*t*-Bu_3)$(CO)_2NO$ (6e) with PMe_3. A solution of **6e** (0.35 g, 1.0 mmol) and PMe_3 (0.11 g, 1.5 mmol) in decane (25 mL) was placed in a 40-mL Fisher-Porter vessel and heated to 80 °C for 18 h. The resultant solution was chromatographed on a Florisil/hexanes column (1 in. × 10 in.). Hexane eluted a small orange band which was evaporated to dryness, leaving an orange solid identified by its IR spectrum as unreacted starting material **6e** (0.08 g). Further elution with CH_2Cl_2 afforded a red orange band. Evaporation and crystallization of the residue from hexanes yielded Fe(η^3-C_3-*t*-Bu_3)(CO)(NO)(PMe_3) (**12b**) as red-orange prisms (0.22 g, 72%): mp 95–97 °C; IR (hexanes) ν_{CO} 1941, ν_{NO} 1704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46 (d, J_{PH} = 7 Hz, 9 H, PMe), 1.21 (s, 27 H, *t*-Bu); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 225.7 (CO), 71.1 (*C*-*t*-Bu), 31.9 (C*Me*$_3$), 31.8 (*C*Me_3), 20.9 (d, J_{PC} = 21 Hz, PMe). Anal. Calcd for $C_{19}H_{36}FeNO_2P$: C, 57.43; H, 9.13; N, 3.52. Found: C, 57.41; H, 9.17; N, 3.49.

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Registry No. **6a**, 82661-42-5; **6b**, 100701-18-6; **6c**, 100701-20-0; **6d**, 100701-22-2; **6e**, 100701-24-4; **7a**, 100896-54-6; **7b**, 100813-53-4; **7c**, 100813-52-3; **7d**, 100813-51-2; **8a**, 100813-50-1; **8b**, 100813-49-8; **8c**, 100896-58-0; **8d**, 100896-55-7; **9a**, 100813-40-9; **9b**, 100839-09-6; **9c**, 100813-41-0; **10a**, 100896-56-8; **10b**, 100897-54-9; **10c**, 100896-57-9; **11a**, 100839-10-9; **11b**, 100813-42-1; **11c**, 100813-46-5; **11d**, 82661-43-6; **11e**, 82661-44-7; **11f**, 100813-43-2; **12a**, 100813-47-6; **12b**, 100813-48-7; **13a**, 100813-44-3; **13b**, 100813-45-4; [P(OPh)$_3$], 101-02-0; [P(OMe)$_3$], 121-45-9; PPh_3, 603-35-0; PMe_2Ph, 672-66-2; PMe_3, 594-09-2.