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Reaction of Benzocyclobutadienedicarbonylnitrosyliron Hexafluorophosphate with R_3M (M = P, As; R = Me, Ph). A Novel Example of a Nucleophilic Addition–Substitution Reaction

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Benzocyclobutadienedicarbonylnitrosyliron hexafluorophosphate has been prepared by the reaction of benzocyclobutadienetricarbonyliron with nitronium or nitrosonium salts in nitromethane solution. The iron nitrosyl complex undergoes facile reaction with 2 mol of R_3M (M = P, As; R = Me, Ph) to afford benzocyclobutenyliron complexes of the type $[(R_3M^+\text{-}\eta^3\text{-}C_8H_6)Fe(CO)(NO)MR_3]PF_6^-$ by a process involving nucleophilic addition–substitution.

Introduction

The coordination properties of tertiary phosphines and related ligands of group 5A elements are well documented.[1] In this context, the substitution reaction of coordinated carbonyl by phosphines and related Lewis bases, of which several hundreds of examples are known, is noteworthy. By contrast, nucleophilic addition of phosphines to acyclic[2,3] or cyclic[4] π ligands is rare, and apart from a few isolated reports, little is currently known about this interesting reaction. Recently, we have described the preparation of (*exo*-phosphonium-η^3-cyclobutenyl)dicarbonylnitrosyliron hexafluorophosphate by the facile reaction of $[C_4H_4Fe(CO)_2NO]^+PF_6^-$ with R_3P (R = Ph, Me, Et, Pr, etc.) and the crystal structure of the trimethylphosphonium derivative.[4] Attempts to affect similar nucleophilic addition reactions with the fully substituted cyclobutadieneiron complexes $[R_4C_4Fe(CO)_2NO]^+PF_6^-$ (R = Me, Ph), or with nucleophiles other than phosphines such as Ph_3As and Ph_3Sb were totally unsuccessful.

In order to extend the knowledge on nucleophilic addition reactions, the partially substituted cyclobutadiene complex benzocyclobutadienedicarbonylnitrosyliron hexafluorophosphate has been prepared and its reactions with nucleophiles have been studied.

Experimental Section

The preparation of the new benzocyclobutadiene- and benzocyclobutenyliron nitrosyl complexes is described below. Microanalyses (Table I) were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Proton NMR spectra were run in acetone-d_6 or CH_3NO_2 solution, as specified in Table II, with TMS as an internal standard on a Jeol JNM-MH-100 spectrometer. ^{31}P NMR spectra (Table III) were run in acetone solution with an external standard of 85% H_3PO_4 solution on a Varian HA100 spectrometer. Infrared spectra (Table III) were taken as KBr pellets and in CH_2Cl_2 solutions on a Perkin-Elmer 225 grating spectrometer. Each spectrum was calibrated using the 1601- and/or 1944-cm^{-1} band of a polystyrene film.

The reagent $C_8H_6Fe(CO)_3$ was prepared by a known procedure.[5] Nitrosonium ($NO^+PF_6^-$) and nitronium ($NO_2^+PF_6^-$) salts were purchased from PCR Inc., Gainesville, Fla.

Nitrogen atmosphere was routinely provided for the following operations: (1) carrying out reactions, (ii) admitting to evacuated vessels, and (iii) handling filtered solutions of organometallic compounds.

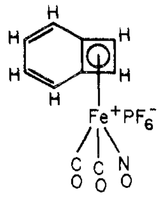
Preparation of $[C_8H_6Fe(CO)_2NO]^+PF_6^-$ (1). A solution of 5.27 g (21.6 mmol) of $C_8H_6Fe(CO)_3$ in 100 ml of nitromethane (Spectra Grade) at 0 °C was treated dropwise over a 30-min interval with a solution containing 3.63 g (19.2 mmol) of $NO_2^+PF_6^-$ in 80 ml of the same solvent. The reaction mixture was allowed to stir for an additional 30 min at ambient temperature and then the solvent was removed on a rotary evaporator at 30 °C (35 mm). The solid obtained was extracted with five 100-ml portions of CH_2Cl_2, the orange extracts were combined and reduced in volume under reduced pressure (35 mm) to ~150 ml, and this solution was treated with ~500 ml of toluene to give 4.70 g of $[C_8H_6Fe(CO)_2NO]^+PF_6^-$ (63% yield). The same iron nitrosyl complex was also obtained (~26%) by using $NO^+PF_6^-$ instead of $NO_2^+PF_6^-$ according to the above procedure.

Preparation of $[(R_3M^+\text{-}\eta^3\text{-}C_8H_6)Fe(CO)(NO)MR_3]PF_6^-$ (2 (M = As, R = Ph; M = P, R = Me, Ph)). 2 (M = As, R = Ph). A solution of 1.17 g (3.8 mmol) of Ph_3As in 150 ml of CH_2Cl_2 was added dropwise over a 30-min interval into a solution containing 0.73 g (1.9 mmol) of $[C_8H_6Fe(CO)_2NO]^+PF_6^-$ in 50 ml of the same solvent at ambient temperature. The reaction mixture was allowed to stir for an additional 15 min and then hexane (~100 ml) was added slowly. The orange reaction mixture was filtered by gravity and the filtrate reduced in volume on a rotary evaporator at 25 °C (35 mm) to afford the bright yellow crystalline product $[(Ph_3As^+\text{-}\eta^3\text{-}C_8H_6)Fe(CO)(NO)AsPh_3]PF_6^-$ (1.26 g, 68%).

The phosphonium derivatives 2 (M = P; R = Me, Ph) were prepared by essentially the same procedure described above for the arsonium analogue. Attempts to prepare the stibonium complex $[(Ph_3Sb^+\text{-}\eta^3\text{-}C_8H_6)Fe(CO)(NO)SbPh_3]PF_6^-$ were unsuccessful. The iron complex 1 does not react with Ph_3Sb in CH_2Cl_2 at ambient temperature while under thermal conditions above 50 °C in 1,1,-2,2-tetrachloroethane solution the starting iron complex decomposes.

Results and Discussion

Benzocyclobutadienetricarbonyliron undergoes a facile reaction with either nitronium (NO_2^+) or nitrosonium (NO^+) in nitromethane solution at 0 °C to afford the benzocyclobutadienedicarbonylnitrosyliron hexafluorophosphate (**1**) complex in 63% and 23% yields, respectively. The main features in the infrared spectrum of **1**, including ν(CO), ν(NO), and ν(PF), closely resemble those of the related iron nitrosyl complexes $[R_4C_4Fe(CO)_2NO]^+PF_6^-$ (**3** (R = H, Me, Ph)),[6] and its proton NMR spectrum consists of two multiplets (4 H, total) and a sharp singlet (2 H) due to the AA'BB' type benzo and cyclobutadiene hydrogens, respectively.



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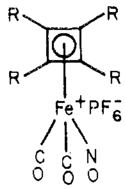


3 (R = H, Me, Ph)

The preparation of **1** with nitrosonium represents an extension of an already known nitrosylation reaction involving the oxidative substitution process I. This synthetic route has

$$(\text{ligands})M\text{–}CO + NO^+ \rightarrow [(\text{ligands})M\text{–}NO]^+ + CO \qquad (I)$$

been utilized successfully to prepare mononitrosyl cationic complexes such as $[M(CO)_{x-1}L_y(NO)]^+$ (L = phosphines),[7] $[R_4C_4Fe(CO)_2NO]^+$ (**3** (R = H, Me, Ph)),[6] $[R_5C_5Mn(CO)_2NO]^+$ (R = H, Me),[8,9] $[(C_6Me_{6-n}H_n)Cr(CO)_2NO]^+$,[10] and $[IrCl(CS)(NO)L_2]^+$ (L = phosphines).[11] By contrast, relatively little is currently known about the nitrosylation reaction with nitronium (II). The nitrosylation reaction with

$$(\text{ligands})M\text{–}CO + NO_2^+ \rightarrow [(\text{ligands})M\text{–}NO]^+ + CO_2 \qquad (II)$$

Table I. New Benzocyclobutadieneiron and Benzocyclobutenyliron Nitrosyl Complexes

Complex	Color	Dec pt,[a] °C	Yield, %	Elemental analysis, % Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
$[C_8H_6Fe(CO)_2NO]^+PF_6^-$ (**1**)	Orange	132	63,[b] 23[c]	30.87	1.55	3.60	31.11	1.49	3.87
$[(Me_3P^+\text{-}\eta^3\text{-}C_8H_6)Fe(CO)(NO)PMe_3]\text{-}PF_6^-$ (**2** (M = P; R = Me))	Yellow	134	53	35.11	4.70	2.70	35.70	4.74	2.59
$[(Ph_3P^+\text{-}\eta^3\text{-}C_8H_6)Fe(CO)(NO)PPh_3]\text{-}PF_6^-$ (**2** (M = P; R = Ph))	Yellow	106	44	61.04	4.10	1.58	60.68	4.09	1.68
$[(Ph_3As^+\text{-}\eta^3\text{-}C_8H_6)Fe(CO)(NO)AsPh_3]\text{-}PF_6^-$ (**2** (M = As; R = Ph))	Yellow	101	68	55.53	3.73	1.44	54.77	3.92	1.51

[a] Uncorrected. [b] From the reaction with $NO_2^+PF_6^-$. [c] From the reaction with $NO^+PF_6^-$.

Table II. Proton NMR Spectra of Some Benzocyclobutadieneiron, Cyclobutadieneiron, and Benzocyclobutenyliron Derivatives

Complex	Proton NMR,[a] τ: Phenyl and/or benzo protons	Cyclobutadiene or cyclobutenyl protons	Methyl protons
$[C_8H_6Fe(CO)_2NO]^+PF_6^-$ (**1**)	2.54 (m, 2 H) 2.70 (m, 2 H)	4.48 (s, 2 H)	
$[C_4H_4Fe(CO)_2NO]^+PF_6^-$ (**3** (R = H))		4.52 (s)	
$[(Me_3P^+\text{-}\eta^3\text{-}C_8H_6)Fe(CO)(NO)PMe_3]\text{-}PF_6^-$ (**2** (M = P; R = Me))	2.95 (m, 2 H) 3.04 (m, 2 H)	4.93 (d, 1 H, J = 10 Hz) 5.59 (d, 1 H, J = 6 Hz)	8.03 (d, 9 H, J = 14 Hz) 8.29 (d, 9 H, J = 10 Hz)
$[(Ph_3P^+\text{-}\eta^3\text{-}C_8H_6)Fe(CO)(NO)PPh_3]\text{-}PF_6^-$ (**2** (M = P; R = Ph))	2.60 (m, 19 H)	4.13 (d, 1 H, J = 6 Hz) 4.78 (d, 1 H, J = 10 Hz)	
$[(Ph_3As^+\text{-}\eta^3\text{-}C_8H_6)Fe(CO)(NO)AsPh_3]\text{-}PF_6^-$ (**2** (M = As; R = Ph))	2.72 (m, 19 H)	4.06 (s, 1 H) 4.56 (s, 1 H)	

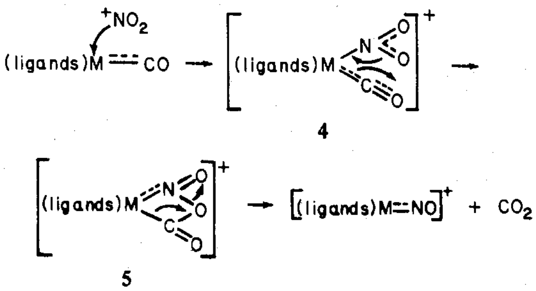
[a] Spectra of **1** and **3** (R = H) were run in CH_3NO_2; those of **2** in acetone-d_6 solution. Abbreviations: s, singlet; d, doublet; m, multiplet.

Table III. Infrared and ^{31}P NMR Data on the New Benzocyclobutadieneiron and Benzocyclobutenyliron Complexes

Complex	Infrared, cm^{-1}: ν_m[a]	$\nu(CO)_{vs}$[a]	$\nu(NO)_{vs}$[a]	$\nu(PF)_{vs}$[b]	^{31}P NMR (ppm rel to 85% H_3PO_4)[c]: $\delta(R_3P)$ s, 1 P	$\delta(R_3P^+)$ s, 1 P	$\delta(PF_6^-)$ t, 1 P
$[C_8H_6Fe(CO)_2NO]^+PF_6^-$ (**1**)		2130, 2101	1860	835			
$[(Me_3P^+\text{-}\eta^3\text{-}C_8H_6)Fe(CO)(NO)PMe_3]\text{-}PF_6^-$ (**2** (M = P; R = Me))	2016	1947	1735	835	−27	−24	+143
$[(Ph_3P^+\text{-}\eta^3\text{-}C_8H_6)Fe(CO)(NO)PPh_3]\text{-}PF_6^-$ (**2** (M = P; R = Ph))	2024	1956	1737	835	−63	−28	+143
$[(Ph_3As^+\text{-}\eta^3\text{-}C_8H_6)Fe(CO)(NO)AsPh_3]\text{-}PF_6^-$ (**2** (M = As; R = Ph))	2020	1956	1738	835			
$C_8H_6Fe(CO)_2PPh_3$					−76		

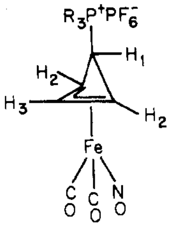
[a] CH_2Cl_2 solution. [b] KBr pellet. [c] Acetone medium. Abbreviations: m, medium; vs, very strong; s, singlet; t, triplet.

nitronium has been tried successfully with carbonyl complexes of the type $QM(CO)_3$ [e.g., M = Fe, Q = C_4H_4; M = Mn, Q = C_5H_5][12] as well as with the thiocarbonyl complexes $RC_5H_4Mn(CO)_2CS$ [R = H, CH_3][13] and appears to be of general application. Occasionally, the nitrosylation reaction with nitronium affords higher yield of product than that with nitrosonium, as in the case of $C_8H_6Fe(CO)_3$. The formation of CO_2, presumed according to process II, has been inferred by its trapping as $BaCO_3$ from $Ba(OH)_2$ solution. Moreover, the nitrosylation of $QM(CO)_3$ [e.g., Q = C_5H_5, M = Mn; Q = C_4H_4, M = Fe] with nitronium, carried out in acetonitrile solution under rigorously anhydrous conditions, has revealed that the products $[QM(CO)_2NO]^+$ and CO_2 (determined gravimetrically as $BaCO_3$) are formed in approximately equimolar ratio. These results suggest that the formation of CO_2 involves oxygen transfer from the nitronium to the coordinated carbonyl. Mechanistically, this reaction is envisaged to proceed via the sequence involving oxidative addition, intramolecular oxygen transfer, and the terminating step of CO_2 elimination, depicted in (III). The intramolecular oxygen-transfer process via electronically and coordinatively saturated intermediates of the types **4** and **5** is likely to be favored over an alternative process involving intermolecular oxygen transfer via unsaturated intermediates, since the former process is expected to afford a lower energy pathway to the products.



(III)

The iron nitrosyl complex **1** undergoes a vigorous exothermic reaction with certain polar organic solvents such as acetone (including acetone-d_6) and acetonitrile. These reactions, which also involve rapid evolution of gas, afford dark paramagnetic solutions whose content could not be determined. The high reactivity of **1** is also evident by its facile reaction with R_3M (M = P, As; R = Me, Ph), in methylene chloride solution at ambient temperature, which affords yellow complexes of the empirical formula $(R_3M)_2C_9H_6NO_2F_6PFe$ (**2** (M = P; R = Me, Ph), **2** (M = As; R = Ph)) and carbon monoxide. The volume of carbon monoxide released during these reactions, measured on a gas buret, was somewhat larger than that expected for the displacement of one carbonyl group from **1**. The larger than expected volume of carbon monoxide measured probably suggests that some decomposition is taking place during the course of these reactions. The reaction between **1** and R_3M appears to involve two steps: the substitution of a carbonyl group in the starting iron complex by R_3M and the nucleophilic addition of R_3M to the benzocyclobutadiene ligand to give a benzocyclobutenyl type complex. The nucleophilic addition step, whether it precedes that involving substitution or vice versa, an issue to be discussed later, is expected to afford a product structurally related to (*exo*-phosphonium-η^3-cyclobutenyl)dicarbonylnitrosyliron hexafluorophosphate (**6**).[4] Therefore, the alternative structures **2a** and **2b**, with the entering nucleophile occupying an exo position with respect to the iron atom, will both be considered for the new complexes (**2**) in light of the various spectroscopic data, discussed below.



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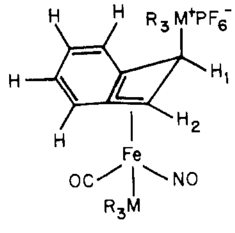
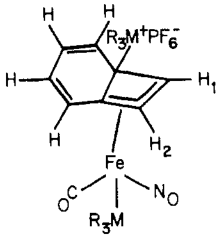


2a



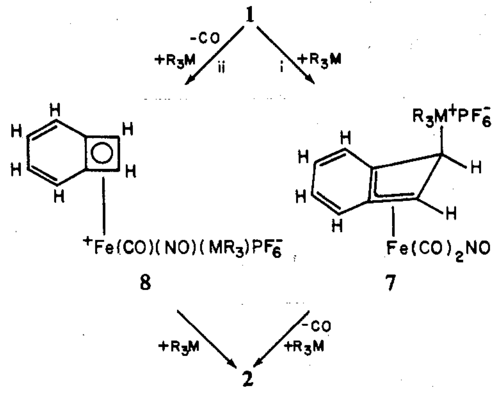
2b

The spectroscopic properties of the new complexes **2** are summarized in Tables II (proton NMR data) and III (^{31}P NMR and selected infrared data). The ^{31}P NMR spectra of **2** (M = P; R = Me, Ph) (Table III), which consist of two singlets (1 P, each) and a high-field triplet (1 P), support the presence of three types of phosphorus atoms in these molecules. The high-field triplet at about δ +143, in both spectra, is due to the P(phosphate) atom with J(PF) = 688 Hz. The observed triplet instead of the expected heptet for PF_6^- is attributed to resolution and solubility limitations. In the spectrum of **2** (M = P; R = Ph) the singlets at δ −63 and −28 are assigned to P(coordinated phosphine) and P(phosphonium) atoms, respectively. These assignments are supported by the singlets at δ −76 and −16 which have been observed in the spectra of the related iron complexes $C_8H_6Fe(CO)_2PPh_3$ (Table III) and **6** (R = Ph),[4] respectively. Similar considerations lead to the assignment of the singlets at δ −27 and −24 in the spectrum of **2** (M = P; R = Me) to the P(coordinated phosphine) and P(phosphonium) atoms, respectively.

The proton NMR spectra of **2** (M = P, As; R = Ph) (Table II) in the aromatic proton region show multiplets (19 H) due to the phenyl and benzo protons, while the ABCD type benzo protons in **2** (M = P; R = Me) give rise to two multiplets (4 H, total). In the spectra of **2** (M = P, As; R = Ph) the cyclobutenyl protons give rise to two resonances which are of similar chemical shifts but of different multiplicity: singlets for the arsine derivative and doublets with different couplings for the phosphine analogue. A similar comparison between the spectra of the phosphine derivatives **2** (M = P; R = Me, Ph) reveals resonances of the same multiplicity, two doublets with different couplings (6 and 10 Hz), of somewhat different chemical shifts (Table II). The absence of $^1H-^1H$ vicinal coupling between the adjacent protons of the cyclobutenyl ring in **2** (M = As; R = Ph), which has also been presumed for the phosphine derivatives **2** (M = P; R = Me, Ph) since the doublets in their spectra are of different couplings, is in agreement with similar data on related cyclobutenylmetal systems reported elsewhere.[4,14,15] The doublets observed in the spectra of the phosphine derivatives are presumed to be due to P–H couplings and there are several such interactions to be considered on the basis of structures **2a** and **2b**. Couplings between the phosphorus atom of the coordinated phosphine and the hydrogen atoms bonded to π ligands, such as $J(P-H_2)$ in **2a** and $J(P-H_1)$ and $J(P-H_2)$ in **2b**, are expected to be 2 Hz or less. These values are suggested on the basis of the proton NMR data available on complexes such as $[C_5H_5Mn(CO)(NO)L]^+PF_6^-$,[16] $C_5H_5Mn(CO)(CS)L$ (L = phosphines),[17] and $[C_4H_4Fe(CO)(NO)PPh_3]^+PF_6^-$.[6] Therefore, the couplings of 6 and 10 Hz observed in the spectra of the phosphine derivatives (**2**) probably represent $J(P^+-H_2)$ and $J(P^+-H_1)$, respectively, according to either **2a** or **2b**. The values of the couplings are in favor of structure **2a** because of the similar $J(P^+-H_1)$ values of 12–14 Hz which have previously been observed in the proton NMR spectra of the related iron complexes **6** (R = Me, Et, *n*-Pr, *n*-Bu, Ph, etc.).[4] Noteworthy in the spectra of the phosphine derivatives **2** (M = P) are the somewhat broader doublets with J = 6 Hz than those with J = 10 Hz which according to structure **2a** could be due to weak coupling with the coordinated phosphine, $J(P-H_2) < 1$ Hz. In view of the above considerations, the resonances at τ 4.56, 4.78, and 4.93 in the spectra of **2** (M = As; R = Ph), **2** (M = P; R = Ph), and **2** (M = P; R = Me), respectively, have been assigned to H_1 and those at τ 4.06, 4.13, and 5.59 in the respective spectra to H_2, according to structure **2a**. The chemical shifts of H_1, bonded to a sp^3 carbon atom of the cyclobutenyl ring, appear to be affected by the nature of the R_3M^+ moiety to a lesser degree than those of H_2 by the coordinated R_3M group. In part, this may be due to the magnetic anisotropy of the iron $d\pi$ orbitals which affects the shielding of H_2 and depends, among others, on the nature of the coordinated R_3M group. The greater basicity of Me_3P than that of Ph_3M (M = P, As) should cause an increase in the electron density of the iron $d\pi$ orbitals in **2** (M = P; R = Me) as compared with the other derivatives, and this could explain the considerably higher chemical shift of H_2 in the proton NMR spectrum of the methylphosphonium analogue.

The infrared spectra of **2** (Table III) show very strong bands at 1947–1956 and 1735–1738 cm^{-1} which have been assigned as ν(CO) and ν(NO) fundamentals, respectively. These bands in the trimethylphosphonium compound are of somewhat lower frequency than the respective bands of the other derivatives (**2**) and this has been attributed to the greater σ-donor ability of coordinated Me_3P compared with that of Ph_3M (M = P, As). A third, medium-intensity band in the carbonyl region at 2016–2024 cm^{-1} has also been observed in the spectra of **2**, taken as KBr pellets and in CH_2Cl_2 solutions. These bands, although in the region of ν(M–H) fundamentals, are not due to a metal hydride bond as indicated by the absence of any high-field (up to τ +43) resonance in the proton NMR spectra of **2**. Moreover, a weak Fe---H_1 interaction, which may be possible according to structure **2a** by presuming a small dihedral angle in the cyclobutenyl ring, should lower $\nu(C-H_1)$ by only little, however, not enough to account for bands in the 2016–2024-cm^{-1} region. A very strong band at 835 cm^{-1} in the infrared spectra of **2**, characteristic of hexafluorophosphate anion, supports the ionic nature of the new complexes. Comparison between ν(CO) and ν(NO) in **2** and **6**[4] reveals lower frequencies for the former complexes. This observation further supports the presence of coordinated R_3M in **2**.

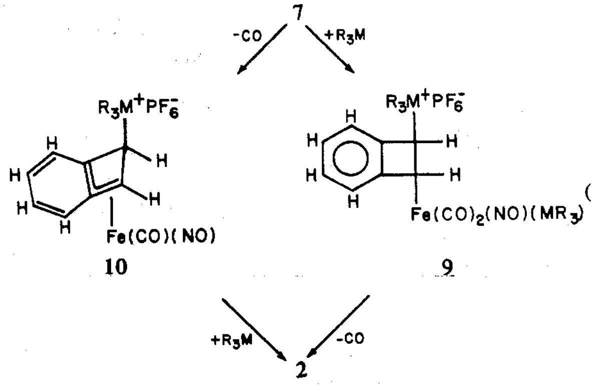
The titration of **1** with R_3M in CH_2Cl_2 solution at ambient temperature, followed by infrared spectroscopy, has revealed the formation of **2** and disappearance of **1** as well as the absence of additional bands in the carbonyl–nitrosyl region due to possible intermediates. Moreover, carbon monoxide evolution during the titration, monitored on a gas buret, has been noticed to be completed within 2–5 s after each addition of R_3M. These results which indicate a relatively fast reaction between **1** and R_3M do not rule out the formation of intermediates with half-life shorter than ~2 s. Mechanistically, the formation of the product **2** may be explained in terms of the sequences involving either addition–substitution (i) or substitution–addition (ii), depicted in (IV). The intermediates



(IV)

7 and **8** considered in (IV) are isoelectronic and structurally related to the stable iron complexes **6**[4] and $[R_4C_4Fe(CO)(NO)PPh_3]^+PF_6^-$ (R = H, Ph),[6] respectively. The facile nucleophilic addition of phosphines to the parent iron nitrosyl complex **3** (R = H), by a process not involving substitution at all, may favor pathway i. However, assuming analogy between **3** (R = H) and **1** could be misleading since the fully substituted complexes **3** (R = Me, Ph) show no tendency to undergo nucleophilic addition reactions with phosphines or related Lewis bases.[4] The nucleophilic addition of R_3M to the cyclobutadiene ring in **1** and **3** (R = H) is likely to depend on the nature of the nucleophile and the electrophilic character of the cyclobutadiene carbon atoms as well as on steric factors. By contrast with the fully substituted cyclobutadieneiron complexes **3** (R = Me, Ph) steric factors are not expected to play a major role in the reactions of **3** (R = H) and **1** with R_3M. Evidently, two of the cyclobutadiene carbon atoms in **1** are sterically unhindered and thus can easily be approached by the entering nucleophile. The relative electrophilicity of the cyclobutadiene carbon atoms in **3** (R = H) and **1** may be judged by comparing the reactions of these complexes with R_3M. Both complexes undergo facile nucleophilic addition of phosphines; however, the addition of Ph_3As has been found to occur only with **1**. These results, taken in the context of the nucleophilicity order R_3P [R = Ph, Me] > Ph_3As, would suggest that the cyclobutadiene carbon atoms in **1** are somewhat more electrophilic than those in **3** (R = H). In the absence of major steric factors, the greater tendency of the cyclobutadiene ligand in **1** compared with that in **3** (R = H) to add nucleophiles of the type R_3M may indirectly support the sequence IV-i. The formation of **2** from **7**, namely, the second step in the addition–substitution sequence, could occur via the σ-benzyl type intermediate **9** or alternatively by the route from the carbonyl-displaced unsaturated intermediate **10**, depicted in V. The former route involving the coordinatively and electronically saturated intermediate **9** is more plausible since it is expected to afford a lower energy pathway to the product.

Noteworthy in particular is the nucleophilic addition of Ph_3As to **1**. This reaction constitutes the first known example of an arsine addition to a π ligand. Moreover, the novel nucleophilic addition reaction between **1** and R_3M, reported herein, appears to be first known case of such a reaction. This interesting reaction has also been studied with tertiary phosphines other than Ph_3P such as Ph_2MeP, $PhMe_2P$, Et_3P, $(n\text{-}Pr)_3P$, and $(n\text{-}Bu)_3P$. The waxy products of these reactions, which could not be purified, give infrared spectra similar to those of **2** (M = P, As; R = Me, Ph) (Table III) in the carbonyl–nitrosyl region. This similarity suggests the structural relationship between the various phosphonium derivatives.



(V)

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Registry No. **1**, 58150-39-3; **2** (M = P; R = Me), 58150-33-7; **2** (M = P; R = Ph), 58150-35-9; **2** (M = As; R = Ph), 58150-37-1; $C_8H_6Fe(CO)_3$, 12093-06-0; Ph_3As, 603-32-7; Me_3P, 594-09-2; Ph_3P, 603-35-0.

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