Contribution from the Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel, and Wright & Rieman Chemistry Laboratories, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903

Nucleophilic Addition of Tertiary Phosphines to Coordinated Cyclobutadiene

AVI EFRATY,* S. S. SANDHU, JR., R. BYSTREK, and D. Z. DENNEY

Received January 28, 1977 AIC70076T

The nucleophilic addition of tertiary phosphines to the coordinated cyclobutadiene in $[C_4H_4Fe(CO)_2NO]^+PF_6^-$ led to the formation of *exo*-phosphoniocyclobutenyldicarbonylnitrosyliron hexafluorophosphate derivatives. The spectroscopic and chemical properties of these novel complexes are described and discussed.

Introduction

The coordination properties of tertiary phosphines and related ligands of group 5A elements are well documented.[1] In this context, noteworthy in particular are the substitution reactions of coordinated carbonyl by phosphines and related Lewis bases of which hundreds of examples are known. By contrast, nucleophilic addition reactions of phosphines and related Lewis bases to acyclic or cyclic π ligands are rather scarce, and apart from several isolated reports, relatively little is currently known about this interesting reaction. Recently, nucleophilic addition of tertiary phosphines to π ligands in certain cationic complexes have been reported to afford a variety of novel phosphonium adducts.[2-10] Similar reactions have very recently also been reported with an arsine[10] and a phosphite[11] ligand.

In order to extend the knowledge on nucleophilic addition reactions, a detailed investigation has been carried out on the reactions between cyclobutadienedicarbonylnitrosyliron hexafluorophosphate (**1**) and various tertiary phosphines.

Experimental Section

The preparation of the new *exo*-phosphonio-η^3-cyclobutenyldicarbonylnitrosyliron hexafluorophosphate complexes (**2**) is described below. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Infrared spectra were recorded on a Perkin-Elmer 225 grating spectrometer. NMR spectra of ^{31}P and ^1H were obtained using Varian-HA-100 and JEOL JNM-MH-100 spectrometers, respectively. Mössbauer spectra were obtained at liquid nitrogen temperature by Professor R. H. Herber of Rutgers University. Conductometric measurements were performed with a YSI Model 31 conductivity bridge and a cell containing platinum black electrodes whose constant was predetermined using a standard solution of KCl. Details concerning the various measurements are furnished in the footnotes of the appropriate tables.

Nitrogen atmosphere was routinely provided for the following operations: (i) carrying out reactions, (ii) admitting to evacuated vessels, (iii) handling solution of organometallic compounds, and (iv) storage of organometallic solids. Solvents used during the course of this investigation were dried, deoxygenated, and freshly distilled before being used. The cationic complex $[(\eta^4\text{-}C_4H_4)Fe(CO)_2NO]^+PF_6^-$ (**1**) was prepared by a known procedure.[12] The tertiary phosphines Me_3P, Et_3P, $n\text{-}Pr_3P$, $n\text{-}Bu_3P$, Ph_3P, Ph_2MeP, and Me_2PhP were purchased from Organomet. Inc., East Hampstead, N.H.

Preparation of $[(exo\text{-Phosphonio-}\eta^3\text{-}C_4H_4)Fe(CO)_2NO]^+PF_6^-$ (2) Complexes. 2 (R = R′ = Ph). A stirred solution containing 2.0 g (5.9 mmol) of $[(\eta^4\text{-}C_4H_4)Fe(CO)_2NO]^+PF_6^-$ in 100 mL of acetone was treated dropwise with an acetone solution (~30 mL) of Ph_3P (1.54 g, 5.9 mmol) over a 30-min interval at ambient temperature (~22 °C). After the addition was completed, the reaction mixture was allowed to stir for about 30 min, the solvent was then removed at 30 °C (35 mm), and the orange product obtained was dried for several hours at 0.1 mm (30 °C). The solid product isolated by this procedure, essentially pure $[(exo\text{-}Ph_3P^+\text{-}\eta^3\text{-}C_4H_4)Fe(CO)_2NO]^+PF_6^-$ (3.5 g, ~100% yield), was recrystallized several times from methylene chloride–toluene mixtures.

2 (R = R′ = Me, Et, *n*-Pr, *n*-Bu; R = Ph, R′ = Me; R = Me, R′ = Ph). These phosphonium analogues of **2** were prepared by essentially the same procedure described above for **2** (R = R′ = Ph). The purification of some of the new complexes, in particular those derived from $n\text{-}Pr_3P$ and $n\text{-}Bu_3P$, required a sequence of recrystallizations from methylene chloride–toluene mixtures at 0 °C.

Attempted Preparation of $[(exo\text{-}Ph_3M^+\text{-}\eta^3\text{-}C_4H_4)Fe(CO)_2NO]^+PF_6^-$ (M = As, Sb). The reactions of Ph_3M (M = As and Sb) with $[(\eta^4\text{-}C_4H_4)Fe(CO)_2NO]^+PF_6^-$ were tried in a variety of polar organic solvents including acetone, acetonitrile, and nitromethane in the temperature range 0–80 °C. At temperatures below ~50 °C, the substrates did not react at all, whereas at higher temperatures the known carbonyl substituted products $[(\eta^4\text{-}C_4H_4)Fe(CO)(NO)L]^+PF_6^-$ (**3**, L = Ph_3As and Ph_3Sb)[12] were obtained in yields ranging from 70 to 86% depending on the experimental conditions.

Thermal Conversion of 2 (R = R′ = Ph) to 3 (L = Ph_3P). The solution of the phosphonium complex **2** (R = R′ = Ph) in a polar organic solvent (e.g., acetone, acetonitrile, nitromethane, etc.) was refluxed for periods ranging from 30 min to 3 h. Under such conditions the starting complex was consumed in its entirety to afford **3** (L = Ph_3P) in yields ranging to a maximum of about 50%.

The other phosphonium analogues of **2** underwent a similar thermal conversion to **3**. Complete characterization of the phosphine derivatives **3** (L = Me_3P, Et_3P, $n\text{-}Pr_3P$, $n\text{-}Bu_3P$, Ph_2MeP, and Me_2PhP) formed in these reactions was hampered due to purification difficulties.

Properties of the New Phosphonium Derivatives 2. The elemental analyses, physical properties, and spectroscopic data of the new complexes, prepared during the course of this investigation, are described in Tables I–IV.

Results and Discussion

The spectral data and physical properties of the new *exo*-phosphoniocyclobutenyldicarbonylnitrosyliron hexafluorophosphate derivatives, prepared by the spontaneous reaction between **1** and phosphines, will be discussed first. The carbonyl and nitrosyl stretching frequencies in the infrared spectra of the new complexes (Table II), which differ only slightly among the analogues, appear at a considerably lower wavenumber than those of **1**.[12] These results are consistent with the presence of a neutral $Fe(CO)_2NO$ moiety in **2**. Moreover, the nature of the phosphonium moiety in **2** appears to have little, if any, influence on the bonding between the iron atom and the ligands around it. The difference in the environment experienced by the iron atom in **2** as compared with that in **1**, or in some of its related derivatives of the type **3**, is evident from the Mössbauer parameters of the complexes under consideration. The IS parameters of the new complexes **2** (Table III) are significantly smaller than those of the cationic complexes **1**[12] and **3** (L = Ph_3P, Ph_3As, and Ph_3Sb);[12] this trend is evidently consistent with the presence of a neutral iron center in **2**. Small, nonetheless significant, differences are found between the IS and QS parameters of the various analogues of **2**. These differences could perhaps be attributed to solid-state effects, since the packing forces of these molecules in the unit cell are expected to be influenced to some degree by the nature of the substituents on the phosphonium moiety in **2**.

The ionic character of **2** which arises from the presence of a phosphonium and PF_6^- ions is clearly evident from the ^{31}P NMR spectra of these complexes (Table II). The low-field singlet [region (δ), −16 to −32 ppm] and the high-field three central lines of the septet [region (δ), +143–144, $J(P\text{–}F)$ = 668 Hz] observed in each of the spectra appear in the regions

---

* To whom correspondence should be addressed at the Weizmann Institute of Science.

Table I. Some (*exo*-Phosphonio-η^3-cyclobutenyl)dicarbonylnitrosyliron Hexafluorophosphate Complexes (**2**)

Complex **2** (R'_2RP)					% elemental analysis[b]											
					Calcd						Found					
R	R′	Color	Mp,[a] °C	% yield	C	H	N	P	F	Fe	C	H	N	P	F	Fe
Me	Me	Red-orange	129–130	83	26.05	3.16	3.37	14.93	27.47	13.46	26.24	3.29	3.37	15.03	27.27	13.72
Et	Et	Red-orange	112–113	72	31.53	4.19	3.06	13.55	24.94	12.2	31.26	4.44	3.08	13.59	25.23	11.95
n-Pr	*n*-Pr	Red	89–90	54	36.09	5.05	2.81	12.41	22.83	11.18	36.05	5.25	2.91	12.64	22.51	10.83
n-Bu	*n*-Bu	Red	109–110	32	39.80	5.72	2.59	11.42	21.05	10.34	39.66	6.02	2.68	11.77	20.85	10.24
Ph	Ph	Orange	118–119	100	17.90	3.08	2.33	10.32	18.90	9.34	47.72	2.94	2.54	9.87	19.30	9.34
Me	Ph	Red-orange	129–130[c]	70	42.30	3.15	2.60	11.50	21.18	10.40	42.90	2.65	2.79	11.22	21.60	11.29
Ph	Me	Red-orange	126	75	35.30	3.13	2.94	13.05	23.80	11.78	35.97	4.42	3.30	12.61	21.95	12.28

[a] Melting points (mp) are uncorrected. [b] Additional data: osmometric molecular weight values for **2** ($P = Ph_3P$) (calcd 601) are 391 (CH_2Cl_2), 433 (acetone), and 493 (pyridine). [c] Decomposition.

Table II. Infrared and ^{31}P NMR data of the new (*exo*-Phosphonio-η^3-cyclobutenyl)dicarbonylnitrosyliron Hexafluorophosphate Complexes (**2**)

Complex **2** (R'_2RP)		Infrared, cm^{-1}				^{31}P NMR,[c] ppm	
R	R′	$\nu(CO)$[a]		$\nu(NO)$[a]	$\nu(PF)$[b]	δ(phosphonium) (s, 1P)	δ(phosphate) (t, 1P, $J(P,F)$ = 668 H)
Me	Me	2068.3	2023.0	1775.7	835	−25 (+62.0)	+144
Et	Et	2068.7	2023.0	1774.3	841	−32 (+20.0)	+144
n-Pr	*n*-Pr	2068.5	2022.0	1773.2	842	−27 (+33.0)	+144
n-Bu	*n*-Bu	2068.0	2022.0	1773.0	838	−28 (+33.0)	+144
Ph	Ph	2070.0	2025.0	1774.0	840	−16 (+5.9)	+143
Me	Ph	2069.4	2024.5	1773.3	841	−19 (+28.0)	+144
Ph	Me	2068.3	2022.8	1774.9	837	−21 (+46.0)	+144

[a] Spectra were recorded in methylene chloride solution on a tenfold expanded abscissa. Each spectrum was individually calibrated against the 1601- and 1944-cm^{-1} bands of a polystyrene film. The reproducibility of these measurements was found to be better than ±0.2 cm^{-1}. [b] Spectra taken as KBr pellets. [c] Spectra were obtained in acetone solution using an external reference of 85% H_3PO_4. The chemical shifts of the free phosphines used in the preparation of the respective complexes, given in parentheses, were taken from ref 13. Abbreviations: s, singlet; t, three central lines of the septet.

Table III. Conductance and Mössbauer Data of the New (*exo*-Phosphonio-η^3-cyclobutenyl)dicarbonylnitrosyliron Hexafluorophosphate Complexes (**2**)

Complex 2 (R'_2RP)		Conductance[a]		Mössbauer parameters,[b] mm/s	
R	R′	λ_0, Ω^{-1}	Slope	IS	QS
Me	Me	118	193	0.116	1.102
Et	Et	116	190	0.088	1.040
n-Pr	*n*-Pr	120	172	0.074	1.031
n-Bu	*n*-Bu	117	180	0.122	1.012
Ph	Ph	95	240	0.097	1.057
Me	Ph	122	164	0.065	1.053
Ph	Me	124	154	0.080	1.035

[a] Measurements were carried out in nitromethane solutions in the concentration range 10^{-2}–10^{-4} M at 26 °C. The molar conductance at infinite dilution (λ_0) was obtained by extrapolation from the λ vs. $c^{1/2}$ curve. The slope was computed from the $\lambda_0 - \lambda$ vs. $c^{1/2}$ curve. [b] The isomer shift (IS) is given with respect to the center of a room temperature absorption of 0.85-mil NBS SRM iron foil, which was also used for velocity calibration. The IS and QS parameters, at temperature ~80 ± 2 K, are estimated to have experimental uncertainties of ±0.015 and ±0.020 mm/s, respectively.

expected[13] for P(phosphonium) and P(PF_6^-), respectively. The low resolution of the septet in the spectra of these complexes has been attributed to solubility limitations. The presence of hexafluorophosphate as a counterion in these complexes (**2**) is also supported by the characteristically strong $\nu(PF)$ band found in the 835–842-cm^{-1} region in the infrared spectra of the complexes. The electrolyte type of the new complexes (**2**) was established by conductometric measurements performed in nitromethane solution. The molar conductances at infinite dilution (λ_0) and slopes $[(\lambda_0 - \lambda)/C^{1/2}]$, determined for the complexes under consideration by extrapolation techniques, are found (Table III) in the expected range for 1:1 electrolytes.[14]

The ^1H NMR spectra of the new complexes **2**, taken in both acetone-d_6 and methylene-d_2 chloride, are given in Table IV. The resonances in these spectra appear in three distinctly different regions (τ), 2.0–2.2, 3.9–6.5, and 7.2–9.0, and these have been assigned to the phenyl, cyclobutenyl, and alkyl protons, respectively. The phenyl protons in the spectra of **2** (R = R′ = Ph; R = Ph, R′ = Me; R = Me, R′ = Ph) give rise to unresolved multiplets, whereas the methyl protons in the spectra of **2** (R = R′ = Me; R = Ph, R′ = Me; R = Me, R′ = Ph) and ethyl protons in the spectrum of **2** (R = R′ = Et) show resonances which are essentially first order with respect to splitting. For example, in the spectrum of **2** (R = R′ = Et), the ethyl protons give rise to a doublet of triplets and a doublet of quartets due to the couplings (Hz) $J(CH_2,CH_3) = 8$, $J(P,CH_2) = 13$, and $J(P,CH_3) = 20$. The chemical shifts and coupling constants of the ethyl protons in the spectrum of this complex are similar to those reported for $Et_4P^+I^-$[15a] and Et_3PO.[15a] In the spectra of **2** (R = R′ = *n*-Pr and *n*-Bu), the methyl protons give rise to a triplet ($J(CH_2,CH_3) = 7$ Hz), while the methylene protons, appearing at lower field, exhibit multiplets whose chemical shifts are increased in the order H(α) < H(β) < H(γ) ($P–CH_2(\alpha)–CH_2(\beta)–CH_2(\gamma)$).

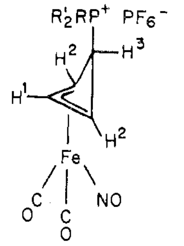
The chemical shifts of the cyclobutenyl protons in the spectra of **2** (Table IV) are similar to those found for the related cyclobutenyliron complexes **4**,[16] **5**[16] and **6**.[17] In the ^1H NMR spectra of **2**, resonances due to the cyclobutenyl protons show the following pattern: a low-field triplet (1 H, $J \approx 4$ Hz), a sharp singlet (2 H, width at half-height <2 Hz), and a high-field doublet of doublets (1 H, $J \approx 4$ Hz, $J' = 10$–14 Hz). These resonances have been assigned to the protons H^1, H^2, and H^3, respectively. The only exception to the indicated pattern has been found in the spectrum of **2** (R = R′ = Ph), taken in acetone-d_6 where the positions of the singlet and triplet are reversed. The multiplicity of the resonances associated with the cyclobutenyl protons might be

Table IV. Proton NMR data of the New (*exo*-Phosphonio-η^3-cyclobutenyl)dicarbonylnitrosyliron Hexafluorophosphate Complexes (**2**)

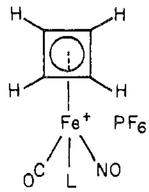
Complex **2** (R'_2RP)		Proton NMR (τ, ppm)[a]							
		Cyclobutenyl			Phosphonium				
R	R′	H^1 (t, 1 H)	H^2 (s, 2 H)	H^3 (d of d, 1 H)	CH_3	CH_2 (α)	CH_2 (β and/or γ)	C_6H_5	Proposed couplings, Hz
Me	Me	3.98 ...	4.43 ...	6.18 ...	7.90 (d, 9 H) ...				$J(1,3) = J(1,P) \approx 4$; $J(3,P) \approx 12$; $J(P,CH_3) \approx 15$
Et	Et	4.03 4.22	4.43 4.87	6.16 6.48	8.61 (d of t, 9 H) 8.67 (d of t, 9 H)	7.46 (d of q, 6 H) 7.69 (d of q, 6 H)			$J(1,3) = J(1,P) \approx 4$; $J(3,P) \approx 10$; $J(CH_2,CH_3) \approx 8$; $J(P,CH_2) \approx 13$; $J(P,CH_3) \approx 20$
n-Pr	*n*-Pr	3.98 4.22	4.43 4.88	6.17 6.50	8.88 (t, 9 H) 8.82 (t, 9 H)	7.57 (m, 6 H) 7.82 (m, 6 H)	7.94 (m, 6 H) 8.34 (m, 6 H)		$J(1,3) = J(1,P) \approx 4$; $J(3,P) \approx 12$; $J(CH_2,CH_3) \approx 7$
n-Bu	*n*-Bu	3.89 4.19	4.31 4.82	6.08 6.47	9.00 (t, 9 H) 8.99 (t, 9 H)	7.45 (m, 6 H) 7.74 (m, 6 H)	8.33 (m, 12 H) 8.40 (m, 12 H)		$J(1,3) = J(1,P) \approx 4$; $J(3,P) \approx 13$; $J(CH_2,CH_3) \approx 7$
Ph	Ph	4.62 4.84	4.44 4.96	4.81 5.51				2.02 (m, 15 H) 2.13 (m, 15 H)	$J(1,3) = J(1,P) \approx 4$; $J(3,P) \approx 14$
Me	Ph	4.47 4.48	4.62 4.84	5.51 5.85	7.21 (d, 3 H) 7.45 (d, 3 H)			2.15 (m, 10 H) 2.03 (m, 10 H)	$J(1,3) = J(1,P) \approx 4$; $J(3,P) \approx 13$; $J(P,CH_3) \approx 13$
Ph	Me	4.30 4.36	4.55 4.91	5.98 6.25	7.53 (d, 6 H) 7.76 (d, 6 H)			2.04 (m, 5 H) 2.03 (m, 5 H)	$J(1,3) = J(1,P) \approx 4$; $J(3,P) \approx 13$; $J(P,CH_3) \approx 14$

[a] Spectra were obtained in acetone-d_6 (top row) and methylene-d_2 chloride (bottom row) solutions using Me_4Si as an internal reference. The estimated accuracy of the data is $\tau \pm 0.02$ ppm and $J \pm 0.5$ Hz. Abbreviations: s, singlet; m, multiplet; t, triplet; q, quartet; α, β, and γ stand for $P-CH_2(\alpha)-CH_2(\beta)-CH_2(\gamma)-CH_3$.

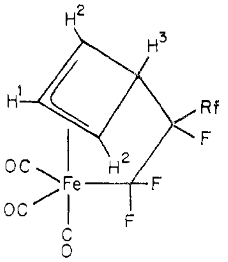
explained by assuming the absence of vicinal and H^2–H^2 transannular couplings and by considering the relationships $J(P,H^1) \approx J(H^1,H^3) < J(P,H^3)$. These assignments are consistent with available ^1H NMR spectral data on cyclobutenyliron complexes as well as on certain relevant phosphine derivatives. Transannular couplings of the type $J(H^2,H^2)$ have so far been encountered only in cyclobutenyl complexes which do not possess a plane of symmetry such as **4** (Rf = CF_3) (10 Hz)[16] and **6** (9 Hz).[17] Incidentally, this behavior is similar to that found for cyclobutadienemetal complexes.[18] The heteronuclear couplings in the spectra of **2** assigned as $J(P,H^3)$ (10–14 Hz) and $J(P,H^1)$ (~4 Hz) are in the expected ranges for P(phosphonium)–H spin–spin interaction across two and four bonds, respectively.[15a] By contrast, the assignment of $J(H^1,H^3)$ (~4 Hz) is considerably more difficult to explain, since it involves interproton coupling interaction across four bonds. In general, long-range interproton coupling interaction across four bonds is known to be rather substantial in cases of rigid and strained systems.[15b] The relatively large $J(H^1,H^3)$ found for **2** and the absence of similar couplings in the spectra of **4** and **5** could probably be attributed to the configuration of the H^3 proton in the complexes under consideration. The endo-H^3 configuration found in **2**[19] suggests the possibility of long-range $H^1 \cdots H^3$ coupling interaction occurring via the π-cyclobutenyliron bonding network. Evidently, this explanation is consistent with the absence of $J(H^1,H^3)$ in the spectra of **4** and **5** in which an exo-H^3 configuration has been postulated.



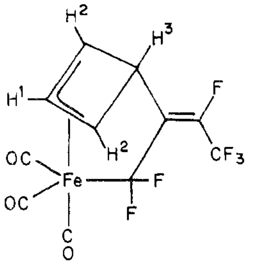
2



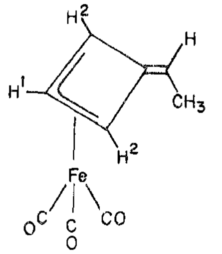
3, L = Ph_3P, Ph_3As, Ph_3Sb



4, Rf = F, CF_3



5

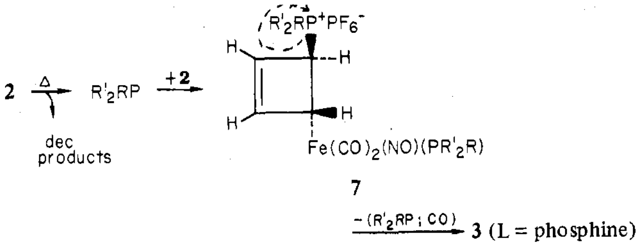


6

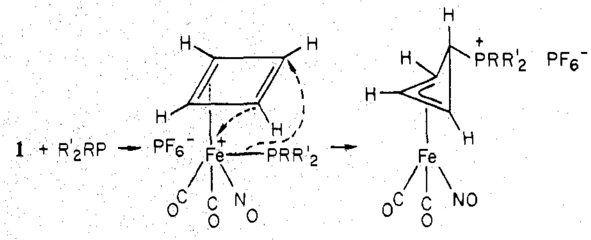
The solvent effect on the chemical shifts of the cyclobutenyl protons in **2** is evident from the data (Table IV). The chemical shifts (τ) of H^1, H^2, and H^3 in spectra taken in acetone-d_6 are found to be consistently at lower field than those of the respective protons in spectra obtained in methylene-d_2 chloride. In part, the observed differences might be attributed to the greater polarity as well as the larger diamagnetic anisotropy associated with the former solvent. Specially interesting in the spectra of these complexes are the relationships between the nature of the phosphonium substituents and the chemical shifts.

The facile addition of tertiary phosphines to the cyclobutadiene ring in **1** to afford **2** contrasts with the failure to effect similar reactions with related bases such as arsines and stilbines. Furthermore, attempts to effect the nucleophilic addition of tertiary phosphines to the fully substituted cyclobutadiene rings of the isoelectronic and isostructural cationic complexes $[R_4C_4Fe(CO)_2NO]^+PF_6^-$ (R = Me, Ph) were also apparently unsuccessful. The only other known case of nucleophilic addition of tertiary phosphines to a coordinated cyclobutadiene ligand has been reported in the instance of the cationic benzocyclobutadieneiron complex $[C_8H_6Fe-$

$(CO)_2NO]^+PF_6^-$.[10] In this particular case, the nucleophilic addition of both phosphines and arsines was shown to be followed by a second step involving carbonyl substitution to afford $[(R_3M^+\text{-}\eta^3\text{-}C_8H_6)Fe(CO)(NO)MR_3]PF_6^-$ (M = P, As; R = Me, Ph). During the current investigation, only the nucleophilic addition step to afford **2** has been encountered, and this took place even when the starting complex **1** was allowed to react with a large excess of the tertiary phosphines. Under mild thermal conditions, for instance in boiling acetone, the reactions of **1** with the Lewis bases (L) Ph_3P, Ph_3As, and Ph_3Sb gave the respective monocarbonyl substituted products **3**.[12] The phosphoniocyclobutenyliron derivative **2** (R = R′ = Ph) was converted under similar thermal conditions to **3** (L = Ph_3P) in a maximum yield of about 50%. The other analogues of **2** underwent a similar thermal conversion to **3**; however, the complete characterization of these new phosphine derivatives was hampered by purification difficulties. The mechanism of conversion of **2** to **3** is not entirely clear. An intramolecular conversion process is highly improbable in view of the exo configuration of the phosphonium moiety in these complexes. Another mechanism involving the initial dissociation of the phosphonium moiety to give equimolar quantities of **1** and free phosphine, which then react thermally to afford the carbonyl-substituted product **3**, is also doubtful. Evidently, in this instance the yield of the ultimate conversion product would have been expected to be higher than a maximum of 50%, as was observed in the analogous reactions between **1** and Ph_3As and Ph_3Sb where nucleophilic addition is not taking place at all.[12] The observed results might be best explained in terms of a sequence involving a slow step of thermal decomposition by which free phosphine is being generated first, followed by a fast thermal reaction between the free phosphine and the excess of **2** to afford the ultimate conversion product **3**, probably via an intermediate of the type **7**. Incidentally, this proposed mechanism of conversion is consistent with the presence of free phosphine and the total absence of either **1** and/or **2** among the products of this interesting thermal reaction.



The rates of addition of $n\text{-}Bu_3P$ to the tropylium ring in the cationic complexes $[(\eta^7\text{-}C_7H_7)M(CO)_3]^+$ (M = Cr, Mo, and W) have recently been shown[20] to obey the rate law: rate = $k[\text{complex}][n\text{-}Bu_3P]$. Based on the kinetics of these reactions, it was argued that the phosphine added directly to the tropylium ligand. It is almost certain that the reactions under consideration between **1** and phosphines proceed via a similar mechanism. An alternative mechanism involving initial rate-determining attack by the phosphine at the iron atom site followed by rearrangement to the cyclobutadiene ring can be ruled out in view of the stereochemical nature of the products. Evidently, such a process would have favored the formation of the *endo*-phosphoniocyclobutenyliron complexes **8**, instead of the observed *exo*-phosphoniocyclobutenyliron configuration of **2** which in the instance of **2** (R = R′ = Me) was confirmed by an x-ray crystal structure analysis.[4]



8

Coordinated cyclobutadiene has been shown to undergo a variety of reactions including electrophilic substitution, nucleophilic substitution, ring expansion, and nucleophilic addition, as well as chemical transformations of the types common in organic syntheses.[18,21] In the context of nucleophilic-addition reactions, noteworthy in particular is the distinction between anionic and neutral nucleophiles. A variety of tetrasubstituted cyclobutadienemetal complexes such as $[Me_4C_4NiCl_2]_2$,[22] $[Ph_4C_4MCl_2]_2$ (M = Pd[23] and Pt[24]), and $[Ar_4C_4MC_5H_5]^+I^-$ (M = Ni, Pd; Ar = aryl)[25] have been shown to undergo facile attack by different anionic nucleophiles (e.g., alkoxides, cyclopentadienide, etc.). By contrast, the addition of neutral nucleophiles has so far been encountered only with the cationic cyclobutadieneiron complexes $[QFe(CO)_2NO]^+$, where Q = cyclobutadiene or benzocyclobutadiene. Analogous iron complexes where Q is a fully substituted ligand (e.g., Me_4C_4 and Ph_4C_4) show no tendency, whatsoever, to add tertiary phosphines or arsines. Current data on the nucleophilic addition of neutral bases to the coordinated cyclobutadiene suggest that these reactions depend rather markedly on the basicity of the nucleophile and electrophilic character of the cyclobutadiene ring carbon atoms as well as on steric factors. Insofar as the coordinated cyclobutadiene ligands are concerned, available experimental data reveal the following decreasing order of ring susceptibility toward the addition of neutral nucleophiles of the type R_3M (R = alkyl and/or aryl; M = P and As): benzocyclobutadiene > parent cyclobutadiene >>> tetrasubstituted cyclobutadiene.

Further studies aimed at establishing the relationships between the various factors influencing the addition of neutral nucleophiles to the coordinated cyclobutadiene ligands are currently in progress and will be reported in due course.

Acknowledgment. This research program was supported in part by the School of Chemistry and the Research Council of Rutgers, the State University of New Jersey. The research work described in this paper was performed at Rutgers College.

Registry No. **2** (R = Me, R′ = Me), 53062-47-8; **2** (R = Et, R′ = Et), 63599-34-8; **2** (R = *n*-Pr, R′ = *n*-Pr), 63599-36-0; **2** (R = *n*-Bu, R′ = *n*-Bu), 63599-38-2; **2** (R = Ph, R′ = Ph), 53062-45-6; **2** (R = Me, R′ = Ph), 63599-40-6; **2** (R = Ph, R′ = Me), 63599-42-8; $[(\eta^4\text{-}C_4H_4)Fe(CO)_2NO]^+PF_6^-$, 43175-64-0.

References and Notes

(1) G. Booth, *Adv. Inorg. Chem. Radiochem.*, **6**, 1–69 (1964).
(2) J. Evans, D. V. Howe, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*, **61**, C48 (1973).
(3) T. H. Whitesides, R. W. Arhart, and R. W. Slaven, *J. Am. Chem. Soc.*, **95**, 5792 (1973).
(4) A. Efraty, J. Potenza, S. S. Sandhu, Jr., R. Johnson, M. Mastropaolo, R. Bystrek, D. Z. Denney, and R. H. Herber, *J. Organomet. Chem.*, **70**, C24 (1974).
(5) P. Hackett and G. Jaouen, *Inorg. Chim. Acta*, **12**, L19 (1975).
(6) D. A. Sweigart and L. A. P. Kane-Maguire, *J. Chem. Soc., Chem. Commun.*, 13 (1976).
(7) D. A. Sweigart, M. Gower, and L. A. P. Kane-Maguire, *J. Organomet. Chem.*, **108**, C15 (1976).
(8) A. Salzer, *Inorg. Chim. Acta*, **17**, 221 (1976).
(9) A. Salzer, *Inorg. Chim. Acta*, **18**, L31 (1976).
(10) A. Efraty, D. Liebman, J. Sikora, and D. Z. Denney, *Inorg. Chem.*, **15**, 886 (1976).
(11) G. R. John and L. A. P. Kane-Maguire, *J. Organomet. Chem.*, **120**, C45 (1976).
(12) A. Efraty, R. Bystrek, J. A. Geaman, M. H. A. Huang, and R. H. Herber, *J. Organomet. Chem.*, **55**, C33 (1973); A. Efraty, R. Bystrek, J. A. Geaman, S. S. Sandhu, Jr., M. H. A. Huang, and R. H. Herber, *Inorg. Chem.*, **13**, 1269 (1974).
(13) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5** (1967), and pertinent references therein.

(14) R. G. Hayter and F. S. Humiec, *Inorg. Chem.*, **2**, 306 (1963).
(15) L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, New York, N.Y., 1969: (a) pp 351–356; (b) pp 334–341; and pertinent examples and/or references therein.
(16) A. Bond and M. Green, *J. Chem. Soc., Dalton Trans.*, 763 (1972); *Chem. Commun.*, 12 (1971).
(17) R. Pettit, J. D. Fitzpatrick, and L. Watts, *Tetrahedron Lett.*, 2069 (1966).
(18) A. Efraty, *Chem. Rev.*, **77**, 691 (1977), an extensive review on cyclobutadienemetal complexes.
(19) A manuscript describing the x-ray crystal structure of **2** (R = R′ = Me) is currently under preparation. For preliminary results see ref 4.
(20) G. R. John, L. A. P. Kane-Maguire, and D. A. Sweigart, *J. Organomet. Chem.*, **120**, C47 (1976).
(21) R. Pettit, *J. Organomet. Chem.*, **100**, 205 (1975), and pertinent references therein.
(22) R. Criegee, F. Förg, H. A. Brune, and D. Schonleber, *Chem. Ber.*, **97**, 3461 (1964); R. Criegee and P. Ludwig, *ibid.*, **94**, 2038 (1961).
(23) D. F. Pollock and P. M. Maitlis, *J. Organomet. Chem.*, **26**, 407 (1971), and pertinent references therein.
(24) F. Canziani, P. Chini, A. Quarta, and A. Dimartin, *J. Organomet. Chem.*, **26**, 285 (1971).
(25) P. M. Maitlis, A. Efraty, and M. L. Games, *J. Am. Chem. Soc.*, **87**, 719 (1965).

Contribution from the Departments of Chemistry, University of Vermont, Burlington, Vermont 05401,
and University of North Carolina, Chapel Hill, North Carolina 27514

Magnetic Exchange in a Chloride- and Adeninium-Bridged Linear Trimer of Copper(II): Octachlorobis(adeninium)tricopper(II) Tetrahydrate

DAVID B. BROWN,*[1a] JOHN R. WASSON,[1b] JAMES W. HALL,[1b] and WILLIAM E. HATFIELD*[1b]

Received May 2, 1977 AIC70309G

Magnetic susceptibility measurements on a powdered sample of the linear trimer octachlorobis(adeninium)tricopper(II) have revealed exchange coupling which may be described by the pairwise Hamiltonian $-2J \sum_{i\neq j} \vec{S}_i\cdot\vec{S}_j$. The exchange integral for the coupling between adjacent copper ions is calculated to be -16.1 cm^{-1} when the exchange between terminal ions in the trimer is set equal to zero. The exchange mechanism is described in terms of the orbital pathways which are available and the single-ion ground-state wave functions.

Introduction

In recent years the study of electron spin exchange interactions in magnetically condensed inorganic materials has progressed rapidly. Certainly the greatest effort and success have been in the study of dimeric complexes, particularly dimeric copper(II) complexes. The theory appropriate for such materials is found to be generally adequate for the description of the magnetic properties. Recently, it has been shown that it is possible to understand the nature and magnitude of the exchange interactions in terms of the chemical and structural features of the molecular system, particularly in the case of hydroxo-bridged copper(II) complexes.[2,3]

Although the magnetic properties of both dimeric and polymeric copper(II) complexes have been examined extensively, there has been relatively little work on oligomeric copper(II) complexes with more than two copper ions, primarily due to a lack of suitably characterized compounds. Since models of the magnetic behavior of oligomeric compounds must ultimately merge as the number of interacting ions increases from two in the simple dimers to large numbers in linear chain compounds, it is desirable to examine linearly interacting systems with intermediate numbers of copper ions.

In the course of our studies of complex formation between adenine and copper(II) chloride in acidic solutions we prepared the known complex octachlorobis(adeninium)tricopper(II) tetrahydrate. The molecular structure (Figure 1) of this material had been determined[4] by a single-crystal x-ray diffraction study and found to consist of linear trimers of copper ions bridged by both adeninium and chloride ions. These trimers are, in turn, weakly polymerized by chloride bridges to form a linear polymer. Since the intertrimer interactions are expected to be significantly smaller than the intratrimer interactions[5] and to have only negligible effects on the magnetic properties except at very low temperatures, we began an investigation of the magnetic properties of this material. This is, to the best of our knowledge, the only magnetic investigation which shows completely the effects of the population of the quartet and doublet states.

Experimental Section

Preparation. de Meester and Skapski reported[4] that octachlorobis(adeninium)tricopper(II) tetrahydrate formed in an attempt to recrystallize dichloroadeninecopper(II), but they reported no preparative details except to note that the material crystallizes from ca. 2 M hydrochloric acid as green elongated prisms. Since several previous attempts to prepare this material in these laboratories were unsuccessful, we report in some detail the routes which do lead to its preparation.

(a) Preparation in 2 M Hydrochloric Acid. A 4.0-g sample (23.5 mmol) of copper(II) chloride dihydrate and 1.58 g (11.7 mmol) of adenine (Sigma Chemical Co.) were added to 40 mL of 2 M hydrochloric acid. The solution was heated to boiling and maintained at the boiling point until the volume was approximately 25 mL. The solution was cooled to ca. 5 °C for 2 h and the product isolated by filtration, washed first with 3 M HCl and then acetone, and air-dried; yield, 1.9 g (2.3 mmol, 40%) of pale green powder. Anal. Calcd for $(C_5N_5H_6)_2Cu_3Cl_8\cdot 4H_2O$: C, 14.67; H, 2.46; Cu, 23.29. Found: C, 14.83; H, 2.50; Cu, 23.06. Melting point: ca. 125 °C darkens to brown, ca. 220 °C melts with decomposition.

(b) Alternative Preparations. A 1.35-g sample (10 mmol) of adenine and 2.35 g (14 mmol) of copper(II) chloride dihydrate were dissolved in 30 mL of water containing 12 mmol of HCl. The solution was boiled until the volume was 15 mL, cooled, and filtered giving 0.6 g of mustard-colored powder (subsequently shown to be (adenine)$CuCl_2$). Concentrated HCl (30 mL) was added to the filtrate, and the solution was heated to boiling and left standing overnight. Filtration gave 1.3 g of bright green crystals shown to be (adenine–H)$_2CuCl_4$. The filtrate was boiled to a volume of 15 mL and filtered, giving a small crop of white crystals (adenine·HCl). This filtrate was boiled to a volume of 8 mL. Filtration gave 0.063 g of pale green crystals. This complex appears to be formed as a persistent contaminant in preparations of other adenine–copper complexes. In particular, what appear to be reasonably clean samples of the compound were formed in low yield in almost all reactions in which copper was in significant excess and the acid concentration was between 2 and 8 M. (In these cases the identity of the material as octachlorobis(adeninium)tricopper(II) tetrahydrate was established by its characteristic melting point behavior rather than by chemical analysis.)

Microanalyses were by Integral Microanalytical Laboratories, Inc., Raleigh, N.C.

Magnetic Measurements. Magnetic susceptibility measurements were made on a powdered sample of $(C_5N_5H_6)_2Cu_3Cl_8\cdot 4H_2O$ using a Foner-type vibrating-sample magnetometer[6] operating at 10 kG as described elsewhere.[7] Nickel metal was employed as a susceptibility standard. Measurements were made in the temperature range 2–160 K. The temperatures were measured with a calibrated GaAs diode. Susceptibilities were corrected for the diamagnetism of the substituent