Kinetic Studies on the Reactions of Tricarbonyl(η-cyclo-octa-1,3-diene)-, Tricarbonyl(η-cyclohexa-1,3-diene)-, and Tricarbonyl(η-cyclohepta-1,3,5-triene)-iron Complexes with Triphenylphosphine

By **Brian F. G. Johnson, Jack Lewis,*** and **Martyn V. Twigg,** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

Tricarbonyl(η-cyclo-octa-1,3-diene)iron reacts smoothly with excess of triphenylphosphine *via* a second-order process to form *trans*-[Fe(CO)$_3$(PPh$_3$)$_2$]. At 60 °C in n-heptane: $k_2 = (3{\cdot}15 \pm 0{\cdot}08) \times 10^{-3}$ l mol^{-1} s^{-1}, $\Delta H^\ddagger = 20{\cdot}76 \pm 0{\cdot}22$ kcal mol^{-1}, and $\Delta S^\ddagger = -8{\cdot}0 \pm 0{\cdot}6$ cal K^{-1} mol^{-1}. In contrast, tricarbonyl(η-cyclohepta-1,3-diene)iron and tricarbonyl(η-cyclohexa-1,3-diene)iron do not react with triphenylphosphine under these conditions. The last complex undergoes a CO-dissociative reaction at high temperatures ($\Delta H^\ddagger = 42{\cdot}1 \pm 0{\cdot}8$ kcal mol^{-1} and $\Delta S^\ddagger = 16{\cdot}5 \pm 1{\cdot}8$ cal K^{-1} mol^{-1}) with retention of the olefin. Tricarbonyl(η-cyclohepta-1,3,5-triene)iron is similarly unreactive, but its reaction with triphenylphosphine at 154 °C involves both first- and second-order processes.

PREVIOUSLY we reported[1] the results of a kinetic study on the reactions of a variety of tertiary phosphines and phosphites with a tricarbonyliron derivative of cyclo-octadiene involving a σ,η-allyl mode of bonding. The products of these reactions depend on the ligand concerned. With weakly basic ligands, L, only carbonyl substitution takes place *via* a first-order process, while with more basic ligands a further second-order process is available that leads to loss of the olefin as a transannular ketone and formation of [Fe(CO)$_2$L$_3$]. Subsequently, we examined the course and kinetics of reaction of some [(cyclic olefin)Fe(CO)$_3$] complexes, not containing an iron–carbon σ-bond, with a single nucleophile, triphenylphosphine, in order to evaluate the relative influence of the iron–carbon σ-bond. These results also enable discussion of some of the factors involved in the competition between loss of carbon monoxide and loss of olefin in reactions of these complexes.

EXPERIMENTAL

Materials.—Complexes used in this study were prepared by u.v. irradiation of Fe(CO)$_5$ and the appropriate ligand in benzene. Freshly distilled, pure, samples of [(cod)-Fe(CO)$_3$] and [(cht)Fe(CO)$_3$] were provided by Drs. I. E. Ryder and G. Evans, and [(chd)Fe(CO)$_3$] by Dr. G. Jaouen of this Department; † [(cod)Fe(CO)$_3$] was sublimed (35 °C, 0·01 mmHg) before use. Although relatively stable, all complexes were stored under a dinitrogen atmosphere at −10 °C until required. Triphenylphosphine (Koch–Light) was recrystallised from absolute ethanol and dried *in vacuo* for several days. Other ligands were commercial samples and used as received. Decalin (Harrington) was passed down a column (40 cm) of alumina. n-Heptane (B.D.H.) was distilled from sodium under an atmosphere of dinitrogen.

Kinetic Measurements.—The general procedures employed have been described.[1] Reactant solutions were degassed by two or more freeze–pump–thaw cycles, and unless otherwise stated the atmosphere in the reaction tubes was argon (99·998%). A thermostatted (±0·05 °C) bath of poly(alkylarylglycol) was used for temperatures up to 110 °C. This was not used for experiments requiring higher temperatures because of possible damage to plastic components in the circulation unit. A smaller (*ca.* 1 l) heavily lagged bath containing heat-transfer oil and utilising magnetic stirring, with a mercury-contact thermometer and electronic switching, was used for high-temperature experiments. At 170 °C, temperature control of this bath was within ±0·2 °C. Temperatures were measured with mercury-in-glass thermometers. When total-immersion thermometers were used the usual stem corrections were made.

Reactions were monitored by measuring the absorbance at the highest-frequency peak of the reactant complex in the i.r. carbonyl-stretching region. Spectra of cooled aliquot portions were recorded on a Perkin-Elmer 247 instrument using 1 mm NaCl liquid cells. Pseudo-first-order rate constants (typically [Complex] ≈ 1 × 10^{-3}, [L] ≈ 20 × 10^{-3}—200 × 10^{-3} mol l^{-1}) were obtained from plots of log ($A_t - A_\infty$) against time, where A_t and A_∞ are the absorbances at time t and infinity respectively; A_∞ was effectively zero. These plots were linear for at least three half-lives.

RESULTS AND DISCUSSION

The reactions of [(cyclic olefin)Fe(CO)$_3$] complexes with phosphorus ligands considered in this paper are as in equations (1) and (2). Over the range 50—80 °C,

$$\begin{array}{l} \text{[(cyclic olefin)Fe(CO)}_3\text{]} \xrightarrow[(1)]{k_1} \text{[(cyclic olefin)Fe(CO)}_2\text{L]} \\ \qquad +\text{L} \xrightarrow[(2)]{k_2} trans\text{-[Fe(CO)}_3\text{L}_2\text{]} \end{array}$$

reaction of [(cod)Fe(CO)$_3$], (I), with triphenylphosphine in n-heptane was exclusively as in (2), no [(cod)Fe(CO)$_2$-PPh$_3$] being detected by i.r. spectroscopy. Plots of observed pseudo-first-order rate constants (k_{obs}), obtained at a given temperature, against [PPh$_3$] were linear (see Figure). The second-order rate constants (k_2) were calculated from a least-squares analysis of the results in which each observed rate constant was assumed to have the same constant fractional error. These data, together with the calculated intercepts (k_1) and their associated error limits, are given in Table 1. With the exception of the value of k_1 at 70·3 °C, the k_1 term was indistinguishable from zero at the 95% confidence level. It appears that the results obtained at 70·3 °C are subject to some systematic error that is responsible for the high k_1 value. Even so, its contribution to the observed rate constant is very small compared with the k_2[PPh$_3$] term. The rate law for this reaction may therefore be written as in (3). Activ-

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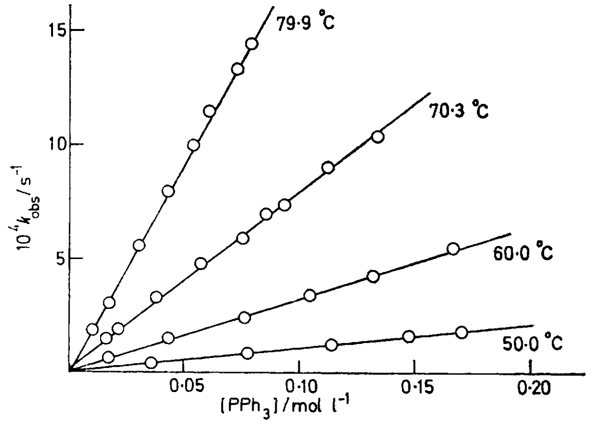
† cod = η-Cyclo-octa-1,3-diene, cht = η-cyclohepta-1,3,5-triene, and chd = η-cyclohexa-1,3-diene.

[1] B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J.C.S. Dalton*, 1974, 241; *J. Organometallic Chem.*, 1973, **52**, C31.

ation parameters for this second-order process, calculated from a weighted least-squares procedure, are

$$-\mathrm{d}[\mathrm{Complex}]/\mathrm{d}t = k_2[\mathrm{Complex}][\mathrm{PPh_3}] \qquad (3)$$

$\Delta H^\ddagger = 20{\cdot}8 \pm 0{\cdot}2$ kcal mol^{-1} and $\Delta S^\ddagger = -8{\cdot}0 \pm 0{\cdot}6$ cal K^{-1} mol^{-1}.*



Plots of k_{obs} against [PPh$_3$] for the reaction of [(cod)Fe(CO)$_3$] with PPh$_3$ in n-heptane

TABLE 1

Kinetic data for reaction of [(cod)Fe(CO)$_3$] with PPh$_3$ in n-heptane

(*a*) Reactions under an argon atmosphere

θ_c/°C	No. [a]	10^5k_1/s^{-1}	10^3k_2/l mol^{-1} s^{-1}
79·9	8	−0·44 ± 0·69	18·34 ± 0·03
70·3	9	1·74 ± 0·60	7·79 ± 0·16
60·0	6	0·72 ± 0·32	3·15 ± 0·08
50·0	5	0·15 ± 0·22	1·05 ± 0·3

Activation parameters [b] for the second-order process are $\Delta H^\ddagger = 20{\cdot}76 \pm 0{\cdot}22$ kcal mol^{-1} and $\Delta S^\ddagger = -8{\cdot}00 \pm 0{\cdot}63$ cal K^{-1} mol^{-1}

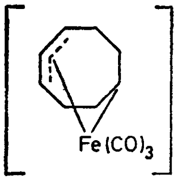
(*b*) Reactions under a carbon monoxide atmosphere at 70·3 °C

[PPh$_3$]/mol l^{-1}	10^4k_{obs}/s^{-1}	10^4k_{calc} [c]/s^{-1}
0·0164	1·40	1·45
0·0870	6·90	6·85

[a] Number of data points. [b] Quoted error limits are standard deviations corrected for the appropriate number of degrees of freedom, such that doubling them produces 95% confidence limits. [c] Calculated by least-mean-squares analysis of results obtained in (*a*) at 70·3 °C.

The relatively high activation enthalpy for a reaction of this type might result from a low degree of bond making in the transition state, as would be expected for the usually poor nucleophile triphenylphosphine.[2] However, the observed activation parameters could be composite values containing terms relating to dissociation of one double bond from the metal atom, if the overall reaction involves this process as a pre-equilibrium rather than direct bimolecular attack on the complex.[3] Indeed, the relatively positive value of the entropy of activation tends to support this suggestion. When the argon atmosphere in the reaction tube was replaced by carbon monoxide (1 atm) the observed rate constants (Table 1) remained unaltered, indicating that loss of carbon monoxide from the complex is not involved in the reaction mechanism. However, [Fe(CO)$_4$PPh$_3$] and *trans*-[Fe(CO)$_3$(PPh$_3$)$_2$] were formed under these conditions, more [Fe(CO)$_4$PPh$_3$] being produced at lower [PPh$_3$]. These observations are consistent with competition of CO and PPh$_3$ for a co-ordinatively unsaturated species.

It is of considerable interest to compare the results for the reaction of complex (I) with triphenylphosphine with those previously obtained for the analogous reaction of tricarbonyl(1-σ,4-6-η-cyclo-octenyl)iron, (II). At 60 °C complex (II) had no detectable second-order reaction with PPh$_3$, a *maximum* upper limit for k_2 being estimated as *ca.* 5×10^{-5} l mol^{-1} s^{-1}, whereas for (I) $k_2 = (320 \pm 10) \times 10^{-5}$ l mol^{-1} s^{-1}. This suggests that the olefin is bound more strongly to the metal in the σ,η-allyl bonding mode, or that there is no readily available mechanism for removal of the olefin when this bonding pattern is employed. It is noteworthy that when the olefin is displaced by reaction with more nucleophilic ligands a ketone is formed.[1] The reactivity of the two complexes is reversed towards loss of carbon monoxide. For complex (I) the experimental conditions used were such that $k_1 \ll k_2[\mathrm{PPh_3}]$. None the less, an upper limit of $k_1 \lesssim 1 \times 10^{-5}$ s^{-1} at 60 °C can be estimated. The corresponding value for (II) is $k_1 = 98 \times 10^{-5}$ s^{-1}. It appears appropriate to assign the reactivity of this complex towards loss of carbon monoxide to the *trans*-influence of the iron–carbon σ-bond. However, the formal oxidation state of iron in complex (II) is two, and zero in (I). Generally, carbon monoxide is not strongly bound in iron(II) complexes.[4]



(II)

The facile displacement of the olefin from (I) under mild conditions by the relatively poor nucleophile PPh$_3$ is also surprising in the light of preparative work on related complexes. Previously, the general conclusion [5] was that thermal displacement of a 1,3-diene from a tricarbonyliron complex by a phosphorus ligand is difficult, but substitution of CO is possible, and further phosphorus ligands only enter the complex with loss of olefin. The general inertness of these complexes towards these ligands is illustrated by the complete recovery of unchanged tricarbonyl(η-cyclohepta-1,3-diene)iron after heating under reflux with PPh$_3$ in benzene for 15 h.[6]

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* 1 cal = 4·184 J, 1 atm = 101 325 Pa.

[2] A. J. Poë and M. V. Twigg, *J. Organometallic Chem.*, 1973, **50**, C39.

[3] F. Zingales, M. Graziani, and U. Belluco, *J. Amer. Chem. Soc.*, 1967, **89**, 256; G. R. Dobson and A. J. Rettenmaier, *Inorg. Chim. Acta*, 1972, **6**, 507.

[4] W. Hieber and K. Wollmann, *Chem. Ber.*, 1961, **94**, 305; I. A. Cohen and F. Basolo, *J. Inorg. Nuclear Chem.*, 1966, **28**, 511.

[5] F. M. Chaudhari and P. L. Pauson, *J. Organometallic Chem.*, 1966, **5**, 73.

[6] J. A. S. Howell, personal communication, 1973.

In order to extend our knowledge of these reactions, the course and kinetics of reaction between [(chd)-Fe(CO)$_3$], (III), and triphenylphosphine was investigated. To obtain convenient reaction times it was necessary to work at considerably higher temperatures than those used for reaction of complex (I), and so the high-boiling hydrocarbon solvent decalin was used instead of n-heptane. The reaction product was identified by i.r. spectroscopy as [(chd)Fe(CO)$_2$PPh$_3$] (Table 2). Similar substitution products were obtained with P(OPh)$_3$, P(OPr^i)$_3$, and PMePh$_2$. Observed pseudo-first-order rate constants for these reactions are given in Table 3. The independence of the observed rate constant on both the nature and concentration of the incoming ligand suggests a CO-dissociative mechanism.

TABLE 2

I.r. data for reactant and product complexes

Complex	Solvent [a]	$\bar{\nu}$(CO) [b]/cm^{-1}
[(cod)Fe(CO)$_3$]	h	2 053, 1 984, 1 980
[(chd)Fe(CO)$_3$]	d	2 045, 1 975, 1 970
[(chd)Fe(CO)$_2${P[(OCH$_2$)$_3$CEt]}]	d	1 998, 1 943
[(chd)Fe(CO)$_2$P(OPh)$_3$]	d	1 996, 1 940
[(chd)Fe(CO)$_2$P(OMe)$_3$]	d	1 982, 1 926
[(chd)Fe(CO)$_2$P(OEt)$_3$]	d	1 977, 1 922
[(chd)Fe(CO)$_2$P(OPr^i)$_3$]	d	1 975, 1 918
[(chd)Fe(CO)$_2$PPh$_3$]	d	1 972, 1 917 [c]
[(chd)Fe(CO)$_2$PMePh$_2$]	d	1 970, 1 915
[(chd)Fe(CO)$_2$PBu$^t{}_3$]	d	1 965, 1 908
[(chd)Fe(CO)$_2$P(C$_6$H$_{11}$)$_3$]	d	1 960, 1 903
[(cht)Fe(CO)$_3$]	d	2 047, 1 983, 1 970
[(cht)Fe(CO)$_2$PPh$_3$]	d	1 979, 1 929
[Fe(CO)$_4$PPh$_3$]	h	2 048,[d] 1 976,[d] 1 942
trans-[Fe(CO)$_3$(PPh$_3$)$_2$]	h	1 889
trans-[Fe(CO)$_3$(PPh$_3$)$_2$]	d	1 889

[a] h = n-Heptane, d = decalin. [b] Recorded on a Perkin-Elmer 247 instrument calibrated with CO. [c] Identical values obtained by photolysis of [(chd)Fe(CO)$_3$] and PPh$_3$ in decalin at 20 °C. [d] Medium intensity, all others strong intensity.

TABLE 3

Pseudo-first-order rate constants for reaction of various nucleophiles with [(chd)Fe(CO)$_3$] in decalin

θ_c/°C	L	[L]/mol l^{-1}	$10^5 k_{obs}$/s^{-1}	$10^5 k_{calc}$ [a]/s^{-1}
157·7	PPh$_3$	0·0607	1·49	1·56
157·7	P(OPh)$_3$	0·0540	1·52	1·56
162·9	PPh$_3$	0·1142	2·94	2·84
162·9	P(OPr^i)$_3$	0·0578	2·84	2·84
169·2	PPh$_3$	0·0626	6·09	5·75
169·2	PMePh$_2$	0·1064	6·35 [b]	5·75
173·4	PPh$_3$	0·0694	9·28	9·11
173·4	PPh$_3$	0·0289	9·63	9·11
178·6	P(OPh)$_3$	0·0475	15·5	15·9
178·6	PPh$_3$	0·1178	15·2	15·9
178·6	PPh$_3$	0·1025	15·5	15·9

Activation parameters were $\Delta H^\ddagger$ = 42·12 ± 0·75 kcal mol^{-1} and $\Delta S^\ddagger$ = 16·5 ± 1·8 cal K^{-1} mol^{-1} (error limits are standard deviations corrected for the appropriate number of degrees of freedom so that doubling them produces 95% confidence limits).

[a] Rate constants calculated from the derived activation parameters. [b] Value not included in calculation of activation parameters (see text).

The activation parameters are consistent with this proposal: the entropy of activation is large and positive.[7] The enthalpy of activation, $\Delta H^\ddagger$ = 42·1 ± 0·8 kcal mol^{-1}, is very large and suggests a strong Fe–CO bond. This is supported to some extent by the reaction not going to completion at 170 °C under an atmosphere of carbon monoxide; at this temperature the equilibrium constant for substitution of CO is small. The rate constant for reaction with the strong[8] nucleophile PMePh$_2$ was 10% higher than that predicted by the other results (Table 3). This possibly indicates there is a small contribution from a second-order reaction with this ligand ($k_2 \approx 5 \times 10^{-5}$ l mol^{-1} s^{-1}), but no evidence for *trans*-[Fe(CO)$_3$(PMePh$_2$)$_2$] was observed in the i.r. spectrum and clearly (III) is very unreactive towards displacement of the olefin by phosphorus ligands.

TABLE 4

Pseudo-first-order rate constants for reaction of [(cht)Fe(CO)$_3$] with PPh$_3$ in decalin at 153·6 °C

[PPh$_3$]/mol l^{-1}	$10^3 k_{obs}$/s^{-1}
0·0348	3·69
0·0552	4·06
0·0797	4·29
0·1065	4·41
0·1300	4·70

k_1 = (3·42 ± 0·16) × 10^{-4} s^{-1}, k_2 = (9·9 ± 2·0) × 10^{-4} l mol^{-1} s^{-1}

TABLE 5

I.r. and kinetic parameters for reaction of some iron complexes with PPh$_3$

Complex	$\bar{\nu}$(CO) [a]/cm^{-1}	Kinetic parameters
[Fe(CO)$_4$PPh$_3$]	2 048m, 1 976m, 1 942s	k_1 = 3 × 10^{-5} s^{-1} (160 °C) [b] $\Delta H^\ddagger$ = 42·5 ± 1·2 kcal mol^{-1} $\Delta S^\ddagger$ = 18·4 ± 2·8 cal K^{-1} mol^{-1}
[(chd)Fe(CO)$_3$]	2 045s, 1 975s, 1 970s	k_1 = 6 × 10^{-5} s^{-1} (163 °C) [c] $\Delta H^\ddagger$ = 42·1 ± 0·8 kcal mol^{-1} $\Delta S^\ddagger$ = 16·8 ± 1·8 cal K^{-1} mol^{-1}
[(cht)Fe(CO)$_3$]	2 047s, 1 983s, 1 970s	k_1 = 3 × 10^{-4} s^{-1} (154 °C) [c] k_2 = 1 × 10^{-3} l mol^{-1} s^{-1} (154 °C) [c]
[(cot)Fe(CO)$_3$]	2 050vs, 1 990s, 1 972s [d]	k_2 = 3 × 10^{-3} l mol^{-1} s^{-1} (127 °C) [e]
[(cod)Fe(CO)$_3$]	2 053s, 1 984s, 1 980s	k_2 = 3 × 10^{-3} l mol^{-1} s^{-1} (60 °C) [c] $\Delta H^\ddagger$ = 20·8 ± 0·2 kcal mol^{-1} $\Delta S^\ddagger$ = −8·0 ± 0·6 cal K^{-1} mol^{-1}
[(1-σ,4—6-η-cod)Fe(CO)$_3$]	2 048s, 1 978s [f]	k_1 = 1 × 10^{-3} s^{-1} (60 °C) [g] $\Delta H^\ddagger$ = 29·2 ± 0·2 kcal mol^{-1} $\Delta S^\ddagger$ = 15·2 ± 0·5 cal K^{-1} mol^{-1}

[a] Recorded in heptane or decalin unless otherwise stated. [b] E. E. Siefert and R. J. Angelici, *J. Organometallic Chem.*, 1967, **8**, 374. [c] This work. [d] Ref. 9; recorded in CCl$_4$. [e] Ref. 9. [f] Unresolved doublet. [g] Ref. 1.

The above results show that the largest cyclic-1,3-diene, cod, is more readily displaced by PPh$_3$ than the smaller rings chd and cyclohepta-1,3-diene. The kinetics of the reaction of [(cot)Fe(CO)$_3$] (cot = η-cyclo-octa-

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[7] R. J. Angelici, *Organometallic Chem. Rev.*, 1968, **3**, 173.

[8] For example, at 60 °C the second-order rate constant for reaction of PMePh$_2$ with Ru$_3$(CO)$_{12}$ is *ca.* 200 times larger than for reaction with PPh$_3$ (M. V. Twigg, unpublished work).

tetraene), (IV), with a variety of phosphorus ligands have been reported.[9] This complex is moderately reactive towards loss of olefin by reaction with PPh_3 ($k_2 = 2{\cdot}8 \times 10^{-3}$ l mol^{-1} s^{-1} at 127 °C), and there is no detectable first-order (k_1) contribution to the observed rate constant under the experimental conditions employed.*

It was of interest to briefly examine the reaction of PPh_3 with a tricarbonyliron complex of a smaller cyclic olefin, having more than two double bonds, but not aromatic. Naïvely, it might be expected to be less reactive towards ligand displacement than (IV) on the basis of the reactivity of the cyclo-1,3-diene complexes. The complex examined was [(cht)Fe(CO)$_3$], (V). Pseudo-first-order rate constants for reaction of this complex with PPh_3 at 154 °C are given in Table 4. At this temperature, loss of CO and formation of [(cht)Fe(CO)$_2$-PPh$_3$] is important [$k_1 = 3{\cdot}4 \times 10^{-4}$ s^{-1}, *cf.* $k_1 = 1{\cdot}5 \times 10^{-5}$ s^{-1} for (III) at 158 °C], while the second-order reaction is considerably less important than for (IV).

Table 5 contains i.r. CO-stretching wavenumbers for all the above complexes and [Fe(CO)$_4$PPh$_3$], together with kinetic data for their reactions with PPh_3. There is no correlation between the wavenumbers and the type of reaction undergone by the complex or even general reactivity. Although there are a few examples of correlation between rate constants and carbonyl-stretching frequencies or force constants, there are many others showing no correlation.[7,10] The similarity of the i.r. wavenumbers in Table 5 is therefore not all together surprising. Enhanced reactivity towards loss of olefin from the tricarbonyliron complexes of the larger cyclic olefins may result from steric factors, although models do not suggest this, or these complexes may have available to them mechanisms involving reactive isomers not available to complexes of the smaller olefins. To enable structure–reactivity trends to become clearly apparent, further results on an extensive range of closely related complexes are required.

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* With the poor nucleophiles $AsPh_3$ and $SbPh_3$, carbonyl-substituted complexes are reported to be obtained in good yield after 15 h at 130 °C. However, three i.r. carbonyl-stretching absorptions rather than the expected two were observed (T. A. Manuel and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 366).

[9] F. Faraone, F. Zingales, P. Uguagliati, and U. Belluco, *Inorg. Chem.*, 1968, **7**, 2362.

[10] R. J. Angelici and C. M. Ingemanson, *Inorg. Chem.*, 1968, **8**, 83; G. R. Dobson and L. A. H. Smith, *ibid.*, 1970, **9**, 1001; R. J. Dennenberg and D. J. Darensburg, *ibid.*, 1972, **11**, 72.