

Hydroxylamines as new decarbonylating reagents in the synthesis of metal carbonyl derivatives

V.A. Maksakov *, V.A. Ershova

Institute of Inorganic Chemistry, Russian Academy of Sciences (RAS), Siberian Branch, Acad. Lavrentyev prosp. 3, Novosibirsk 630090, Russian Federation

Received 12 March 1994; in revised form 20 March 1994

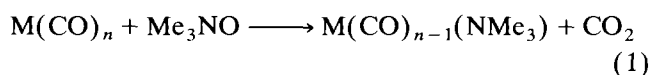
Abstract

Mononuclear and cluster carbonyl complexes react with amino functional compounds under mild conditions in the presence of H_2O_2 to form mixed amino carbonyl derivatives. It was found that a group of reactive species facilitating the process are hydroxylamines which arise in situ as a result of oxidation of amino compounds. On the basis of kinetic data and certain other measurements the mechanism of interaction of $M(CO)_6$ ($M = Cr, Mo, W$) and NH_2OH is proposed. This includes nucleophilic attack by NH_2OH on a carbonyl carbon resulting in CO oxidation and CO_2 elimination with simultaneous intramolecular movement of the amino group to the metal atom. The above mechanism is compared with that for the analogous reaction facilitated by Me_3NO , studied earlier.

Keywords: Chromium; Molybdenum; Tungsten; Osmium; Cluster; Hydroxylamine

1. Introduction

The extensive use of transition metal carbonyl complexes as reagents and catalysts in the synthesis of numerous organic compounds [1] has stimulated parallel advances in carbonyl activation methods. Thermal, photochemical, electrochemical and other technologies may all serve to replace the CO group by another ligand. In the late fifties it was found that some transition metal carbonyls can be oxidized by compounds containing organic N-O-unit such as azobenzenes, nitrosoamines, aminoxides, nitro- and nitroso-compounds [2,3], but the reaction with trimethylaminoxide has been most commonly utilized [4]. In this process trimethylaminoxide participates in oxidizing a carbonyl ligand to give CO_2 followed by addition, to the vacant site, of a ligand present in the reaction mixture [5]



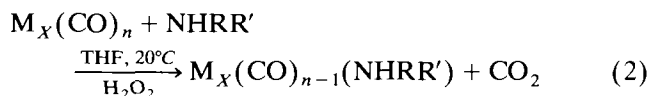
However, still only little is known of the stereochemistry of the direction of CO substitution. At the same time these aspects are of considerable importance in view of mixed-ligand mononuclear and, in particular, cluster complexes in which CO replacement may occur at different metal atoms. We have encountered this problem during the production of enantiomeric trisium clusters whose optical activity is due to asymmetrical arrangement of ligands [6]. The racemic cluster was resolved into enantiomers via the diastereomers, which were obtained as a result of CO replacement by an optically active amino ligand in the presence of Me_3NO .

However, in some cases an attempt to resolve the mixture of diastereomers was unsuccessful. We have found that when H_2O_2 is used in place of Me_3NO as an oxidant the chiral ligand occupies a coordination site other than with Me_3NO to give a separable pair of diastereomers [6]. Using kinetic data, we report here the reactions between several transition metal carbonyl mononuclear and cluster complexes and amino functional compounds in the presence of hydrogen peroxide.

* Corresponding author.

2. Results and discussion

The reaction of transition metal carbonyl mononuclear and cluster complexes with amino functional compounds in the presence of H_2O_2 can be written as follows:



This reaction might be expected to be simply the oxidation of CO to CO_2 followed by amine addition to the vacant coordination site, but this was found not to be so. On the contrary, the cluster $(\mu\text{-H})\text{Os}_3\{\mu\text{-O}=\text{CNHCH}_2\text{CO}(\text{O})\text{Et}\}(\text{CO})_{10}$ (**I**) appears to display no interaction with H_2O_2 in the absence of amine. This conclusion is based on the fact that, when a 10-fold excess of H_2O_2 has been added to a THF solution of **I**, the intensity of the nonoverlapping C=O absorption band at 2105 cm^{-1} is found to be unchanged in the monitoring IR spectrum over at least 6 h. The addition to this mixture of equimolar (relative to H_2O_2) alanine ester led ca. 50% of complex **I** to be converted into $(\mu\text{-H})\text{Os}_3\{\mu\text{-O}=\text{CNHCH}_2\text{CO}(\text{O})\text{Et}\}(\text{CO})_9\{\text{NH}_2\text{CH}(\text{CH}_3)\text{CO}(\text{O})\text{Et}\}$ (**II**) over the same period of time. With glycine ester, ca. 50% of complex **I** is converted into the corresponding complex $(\mu\text{-H})\text{Os}_3\{\mu\text{-O}=\text{CNHCH}_2\text{CO}(\text{O})\text{Et}\}(\text{CO})_9\{\text{NH}_2\text{CH}_2\text{CO}(\text{O})\text{Et}\}$ (**III**) over ca. 2 h, and with amylamine, only a few minutes are sufficient to transfer the same half of the initial complex **I** into $(\mu\text{-H})\text{Os}_3\{\mu\text{-O}=\text{CNHCH}_2\text{CO}(\text{O})\text{Et}\}(\text{CO})_9\{\text{NH}_2(\text{CH}_2)_4\text{CH}_3\}$ (**IV**). Thus, the above data show that the reaction time depends on the nature of the amino species.

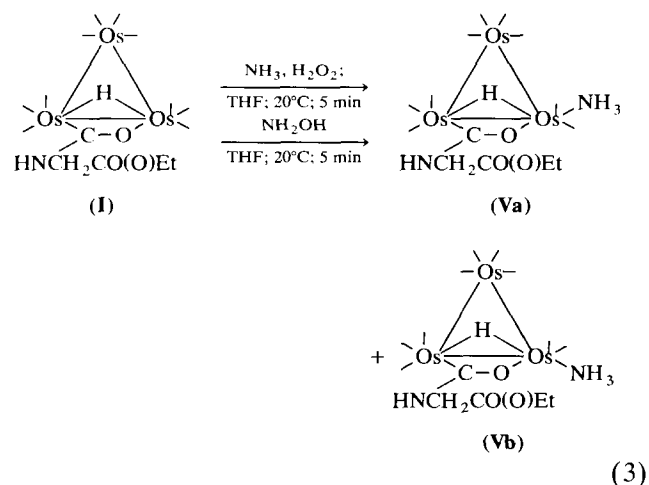
In each case the pair of geometrical isomers **a** and **b** of a new complex may be seen to form. The **a** isomers were found to be less stable and in solution they isomerize to isomers **b** over time. It should be noted that in the analogous reaction when Me_3NO was used, only the **b** isomers are produced. No reaction of complex **I** with PPh_3 is detected in the presence of H_2O_2 in contrast to what is noted with amino functional compounds. Obviously, the cause of facile CO replacement is not immediately hydrogen peroxide, but some product of its interaction with the amino species. It might be hydroxylamine, nitro- or nitroso-compound.

A number of experiments have shown that one species active towards carbonyl oxidation appears to be hydroxylamine. The main evidence has been drawn from comparison of the two parallel processes. In the first process, a THF solution of cluster **I** was treated with NH_2OH , and in the second, through the same initial solution a slow stream of NH_3 was passed and H_2O_2 was added. The reactions were monitored by TLC. After a few minutes, in both cases the same pair of products, $(\mu\text{-H})\text{Os}_3\{\mu\text{-O}=\text{CNHCH}_2\text{CO}(\text{O})\text{Et}\}(\text{CO})_9$

(NH_3) (**Va** and **Vb**), was formed. All compounds were isolated in the individual state. In solution the products with higher R_f (0.42; hexane–ether 5:7 as an eluent), **Va**, are smoothly converted to that with lower R_f (0.32), **Vb**, without decomposition. The IR spectra of both **Va** and **Vb** obtained in the parallel experiments resemble each other and correspond essentially to the spectra of the isomers **a** and **b**, respectively, of clusters **II** and **III**, mentioned earlier [7] (Fig. 1).

The ^1H NMR spectrum of cluster **Vb** differs from that of the starting complex **I** by appearance of the additional broad single resonance ($\delta(\text{NH}_3)$ 3.89 ppm) which overlaps with the multiplet originating from the two CH_2 groups of the bridging ligand (integral intensity 7H). As compared with spectrum of **I**, the singlet arising from the bridging H atom is shifted ca. 0.5 ppm downfield because of attachment of NH_3 to the bridged osmium atom [8]. The mass spectra of the isomers **Va** and **Vb** display the molecular ion peak M^+ 976 (^{192}Os) as well as the peaks corresponding to successive loss of NH_3 and nine CO fragments.

The course of the parallel reactions and the products obtained indicate that in both processes an active agent is apparently found to be NH_2OH , which formed in situ in the second case, and the products represent the isomers



It is believed that the isomerization of cluster **Va** in a similar manner to **IIIa** [7] is due to the pseudoequatorial-equatorial reorientation of NH_3 ligand around the osmium atom attached to the oxygen of the bridging ligand.

The reaction of cluster **I** with N-substituted hydroxylamines such as CH_3NHOH and Et_2NOH (the latter arising in situ from Et_2NH and H_2O_2) proceeds in the same way to give in both cases a pair of isomers $(\mu\text{-H})\text{Os}_3\{\mu\text{-O}=\text{CNHCH}_2\text{CO}(\text{O})\text{Et}\}(\text{CO})_9\{\text{NH}_2\text{CH}_3\}$ (**VIa,b**) and $(\mu\text{-H})\text{Os}_3\{\mu\text{-O}=\text{CNHCH}_2\text{CO}(\text{O})\text{Et}\}(\text{CO})_9\{\text{NH}(\text{C}_2\text{H}_5)_2\}$ (**VIIa,b**). In solution each of the isomers

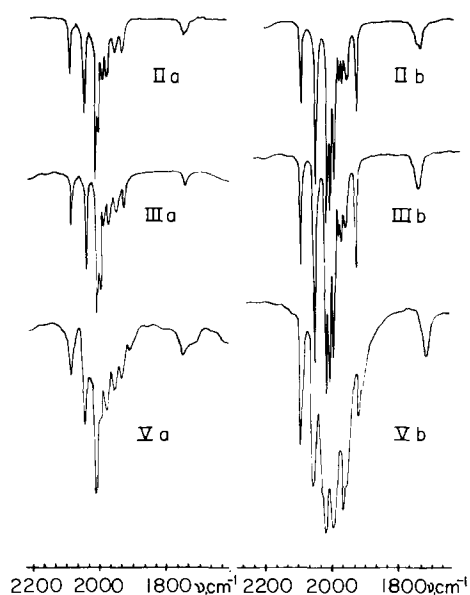
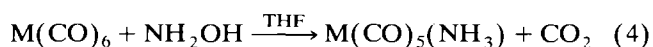


Fig. 1. Infrared spectra in the $\nu(\text{CO})$ region of isomer complexes $(\mu\text{-H})\text{Os}_3\{\mu\text{-OCNHCH}_2\text{CO(O)Et}\}(\text{CO})_9\text{L}$: **IIa**, **IIb**: $\text{L} = \{\text{NH}_2\text{CH}(\text{CH}_3)\text{CO(O)Et}\}$; **IIIa**, **IIIb**: $\text{L} = \text{NH}_2\text{CH}_2\text{CO(O)Et}$; **Va**, **Vb**: $\text{L} = \text{NH}_3$ (**II** and **III** in cyclohexane, **V** in KBr pellet).

a converts into the more stable **b**. On the basis of spectral data (Table 1) we conclude that the isomers formed have the same geometry as complexes **IIIa** and **IIIb**, respectively. The structure of the more stable isomer **Vb** was determined by X-ray structural analysis [9]. As suggested previously on the basis of spectral data, the MeNH_2 molecule has been confirmed to occupy the equatorial position at the osmium atom bound to oxygen of the bridging ligand.

The reaction of the hydroxylamines with complex **I** was extended to other carbonyl cluster and mononuclear compounds. In THF solution, the interaction of $\text{Os}_3(\text{CO})_{12}$ with MeCN in the presence of NH_2OH gave an 81% yield of $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$, which is usually synthesized using Me_3NO as an oxidizing agent [10]. $\text{Ru}_3(\text{CO})_{12}$ reacts readily with hydroxylamine to yield a mixture of products which are difficult to separate.

Mononuclear hexacarbonyls of the VIb group metals $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) react readily with NH_2OH as well. These complexes exhibit behaviour analogous to that of the cluster compounds and, as a result, amino-substituted carbonyl derivatives are obtained.



Reaction 4 offers a convenient synthetic route to such chromium, molybdenum and tungsten amino carbonyl derivatives [11], which can be used further as suitable starting materials in the synthesis of other substituted derivatives of these metals.

In addition, we have examined briefly organic compounds containing N-O-unit-functionalities other than hydroxylamine such as nitro-, nitroso- and oxime functional groups, e.g., CH_3NO_2 , $[\text{Ph-C}(\text{=NOH})\text{-C}(\text{CH}_3)_2\text{-N}=\text{O}]_2$, and $\text{CH}_3(\text{CH}_2)_7\text{-CH}\{\text{-C}(\text{=NOH})(\text{CH}_2)_6\text{CH}_3\}\text{N}(\text{CH}_3)_2$. Under mild conditions all the compounds listed show no interaction with cluster **I** in THF for at least two days. The rather low activity of such compounds towards carbonyl complexes was pointed out earlier [3,12]. The present reaction was reported to occur at an appreciable rate only at elevated temperatures. In summary, it could be concluded, that the reaction of carbonyl complexes with primary and secondary amino functional compounds in the presence of H_2O_2 involves a stage of the carbonyl ligand being oxidized by hydroxylamines, resulting from H_2O_2 -amino-group interaction.

Obviously, the high rates of the carbonyl complex reaction with hydroxylamines as well as with Me_3NO , are caused by the nucleophilic properties of these reagents, and evolution of CO_2 seems to be a result of the nucleophilic attack of the N–O oxygen on the carbonyl carbon atom [5,13,14]. However, the mechanistic details of the interaction of the metal carbonyl complex with hydroxylamines may be discovered only from the kinetic data.

As the model systems we have chosen the simplest ones—Group VIb metal carbonyls as the substrate and NH_2OH as the reagent. The well-defined isosbestic points during the UV-Vis spectral changes of these reactant $\text{M}(\text{CO})_6/\text{NH}_2\text{OH}$ mixtures indicates that the processes are stoichiometric (Fig. 2), and, at the same time, the IR spectra show that the only product, $\text{M}(\text{CO})_5(\text{NH}_3)$, is formed (λ ca. 380 nm, the strongest CO stretching 1928 cm^{-1}).

The observations show that k_1 values depend on the NH_2OH concentration. The plots of k_1 vs. $[\text{NH}_2\text{OH}]$ are linear and pass through the origin (Fig. 3), indicating a first-order dependence of the reaction rate on hydroxylamine concentration. The overall rate expression is followed:

$$-\text{d}[\text{M}(\text{CO})_6]/\text{d}\tau = k_2[\text{M}(\text{CO})_6][\text{NH}_2\text{OH}]$$

Thus, our study of the $\text{M}(\text{CO})_6$ reactions with NH_2OH shows that these processes obey an $\text{S}_{\text{N}}2$ type mechanism as indicated by the first-order kinetics in metal hexacarbonyl and hydroxylamine concentrations. Liberation of carbon dioxide as a result of the reaction suggests nucleophilic NH_2OH attack at the carbonyl carbon atom. The values E_a^{eff} and $\log A_0$ (Table 2) derived from the plots of $\ln(k_2)$ vs. $1/T$ (Fig. 4) are also consistent with an associative mechanism.

Attention is attracted by the fact that k_2 , being only slightly dependent on temperature, results in low values of the effective activation energy E_a^{eff} . The most probable explanation of this phenomenon seems to be

Table 1

IR-, ¹H NMR- and mass spectral data for complex **I** and its derivatives

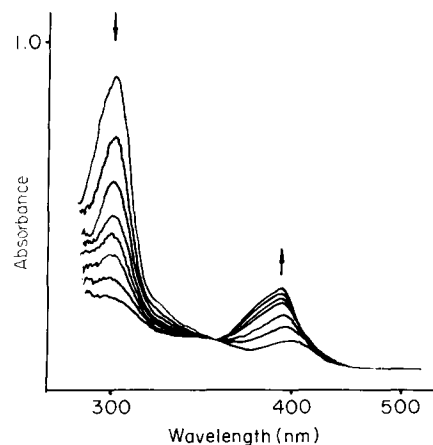
$\nu_{\text{CO}}, \text{cm}^{-1}$	δ, ppm^a	(M ⁺) ^b
(μ -H)Os ₃ { μ -OCNHCH ₂ CO(O)Et}(CO) ₁₀ (I) (cyclohexane)	(CDCl ₃)	987
2106m, 2054vs, 2067vs, 2022vs, 2008vs, 1993s, 1983w, 1977m, 1951vw	6.52 (t, 1H, NH), 4.17 (q, 2H, OCH ₂), 3.84 (m, 2H, CH ₂), 1.21 (t, 3H, CH ₃), -14.25 (s, 1H, μ -H)	
(μ -H)Os ₃ { μ -OCNHCH ₂ CO(O)Et}(CO) ₉ - {NH ₂ CH(CH ₃)CO(O)Et} (IIa1 , IIa2) (cyclohexane)	(CDCl ₃)	1076
2088m, 2044s, 2012vs, 2003s, 1990m, 1979m, 1954w, 1931w	6.64 (t, 1H, NH), 4.27 (m, 5H, 2OCH ₂ , CH), 3.77 (m, br, 2H, NH ₂), 1.35 (m, 9H, 3CH ₃), -20.55 (s, 1H, μ -H)	
(μ -H)Os ₃ { μ -OCNHCH ₂ CO(O)Et}(CO) ₉ - {NH ₂ CH(CH ₃)CO(O)Et} (IIb1 , IIb2) (cyclohexane)	(C ₆ D ₆)	1076
2091m, 2048s, 2013vs, 2004vs, 1992s, 1978m, 1969m, 1955w, 1926m	5.50 (t, br, 1H, NH), 3.97 (m, 5H, 2OCH ₂ , CH), 3.43 (s, br, 2H, NH ₂), 2.68 (m, 2H, NCH ₂), 1.06 (m, 9H, 3CH ₃), -13.61 (s, 1H, μ -H)	
(μ -H)Os ₃ { μ -OCNHCH ₂ CO(O)Et}(CO) ₉ - {NH ₂ CH ₂ CO(O)Et} (IIIa) (cyclohexane)	(CDCl ₃)	1063
2088m, 2044s, 2011vs, 2004s, 1991m, 1975m, 1954w, 1932w	6.55 (t, 1H, NH), 4.15 (m, 4H, 2OCH ₂), 4.02 (d, 2H, NCH ₂), 3.78 (q, 2H, NH ₂ CH ₂), 3.50 (m, br, 2H, NH ₂), 1.29 (m, 6H, 2CH ₃), -20.56 (s, 1H, μ -H)	
(μ -H)Os ₃ { μ -OCNHCH ₂ CO(O)Et}(CO) ₉ - {NH ₂ CH ₂ CO(O)Et} (IIIb) (cyclohexane)	(CDCl ₃)	1063
2090m, 2047s, 2014vs, 2004vs, 1997w, 1992s, 1969m, 1953w, 1926m	6.58 (t, 1H, NH), 4.17 (m, 4H, 2OCH ₂), 4.02 (d, 2H, NCH ₂), 3.70 (q, 2H, NH ₂ CH ₂), 3.54 (m, br, 2H, NH ₂), 1.27 (m, 6H, 2CH ₃), -13.61 (s, 1H, μ -H)	
(μ -H)Os ₃ { μ -OCNHCH ₂ CO(O)Et}(CO) ₉ - {NH ₂ (CH ₂) ₄ CH ₃ } (IVb) (cyclohexane)		1046
2085m, 2042s, 2006vs, 1997s, 1988s, 1972m, 1960m, 1916m		
(μ -H)Os ₃ { μ -OCNHCH ₂ CO(O)Et}(CO) ₉ (NH ₃) (Va) (cyclohexane)		976
2087w, 2071sh, 2044m, 2026sh, 2010s, 1980m, 1956m, 1935w, 1906ws		

Table 1 (continued)

$\nu_{\text{CO}}, \text{cm}^{-1}$	δ, ppm^a	(M ⁺) ^b
(μ -H)Os ₃ { μ -OCNHCH ₂ CO(O)Et}(CO) ₉ (NH ₃) (Vb) (KBr pellet)	((CD ₃) ₂ CO)	976
2092m, 2050s, 2011vs, 1989s, 1959s, 1916m	6.56 (t, br, 1H, NH), 4.07–3.80 (m, 7H, OCH ₂ , CH ₂ , NH ₃), 1.27 (t, 3H, CH ₃), -13.73 (s, 1H, μ -H)	
(μ -H)Os ₃ { μ -OCNHCH ₂ CO(O)Et}(CO) ₉ (NH ₂ CH ₃) (VIb) (CCl ₄)	(CDCl ₃)	990
2093m, 2050s, 2012vs, 2004vs, 1992s, 1977m, 1952m, 1922m	6.39 (s, br, 1H, NH), 4.12 (m, 4H, OCH ₂ , NH ₂) 3.72 (m, 2H, CH ₂) 3.04 (s, 3H, NCH ₃), 1.19 (t, 3H, OCH ₂ CH ₃), -13.63 (s, 1H, μ -H)	
(μ -H)Os ₃ { μ -OCNHCH ₂ CO(O)Et}(CO) ₉ (NHEt ₂) (VIIa) (hexane)	(CCl ₄ /CD ₂ Cl ₂)	1032
2086m, 2044s, 2013vs, 2004vs, 1992m, 1974m, 1953m, 1932m	6.60 (s, br, 1H, OCNH), 4.87 (s, br, 1H, NH Et ₂), 4.02 (m, 4H, CH ₂ , OCH ₂), 3.15 (m, 4H, 2NCH ₂), 1.22 (t, 9H, 3CH ₃), -20.99 (s, 1H, μ -H)	
(μ -H)Os ₃ { μ -OCNHCH ₂ CO(O)Et}(CO) ₉ (NHEt ₂) (VIIb) (hexane)	(CCl ₄ /CD ₂ Cl ₂)	1032
2091m, 2050vs, 2015vs, 2004vs, 1927m	6.52 (t, br, 1H, OCNH), 4.06 (m, 3H, OCH ₂ , NHEt ₂), 3.67 (m, 2H, CH ₂), 3.29 (m, 4H, 2NCH ₂), 1.21 (t, 9H, 3CH ₃), -13.59 (s, 1H, μ -H)	

^a Relative to TMS; ^b corresponded to peaks of isotope ¹⁹²Os.

the solvation of NH₂OH molecules accompanied by hydrogen bond formation to cause some increase of hydroxylamine reactivity. When the solution is heated, the hydrogen bonding is weakened to result in the

Fig. 2. Ultra-violet absorbance changes vs. time for the reaction $\text{W(CO)}_6 + \text{NH}_2\text{OH} \rightarrow \text{M(CO)}_5(\text{NH}_3) + \text{CO}_2$ in diglyme at 25.8°C.

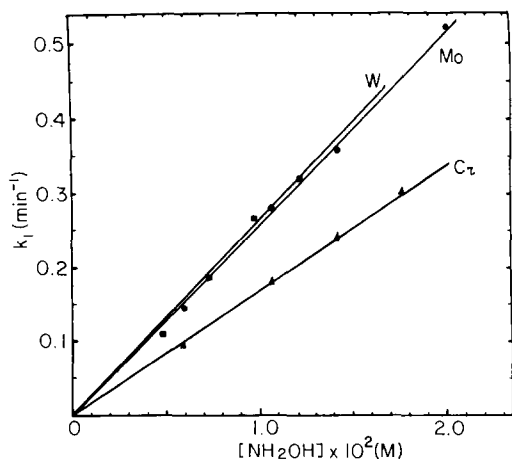


Fig. 3. Dependences of k_1 vs. NH_2OH concentration for the reaction $\text{W}(\text{CO})_6 + \text{NH}_2\text{OH} \rightarrow \text{M}(\text{CO})_5(\text{NH}_3) + \text{CO}_2$ in diglyme at 25.8°C .

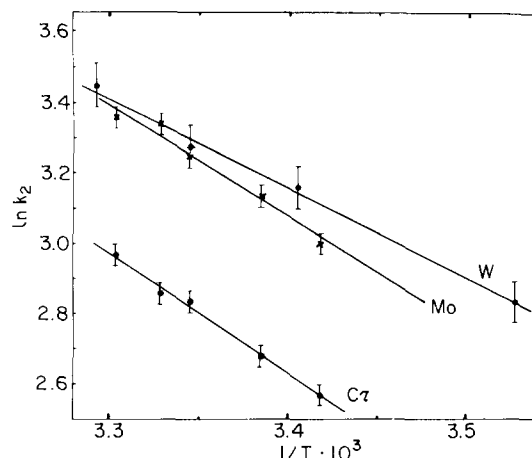


Fig. 4. Plots of $\ln k_2$ vs. $1/T$ for the reaction $\text{M}(\text{CO})_6$ with NH_2OH in diglyme.

share of the active solvated NH_2OH form being reduced. Therefore, k_2 values are thought to be effective but not real because of a preequilibrium constant contribution owing to such hydroxylamine activation processes.

The unstable intermediate $[(\text{CO})_5\text{M}(\text{CO}_2\text{H}\text{NH}_2)]$, believed to form at the first reaction stage, can be stabilized further by alternative pathways. In the first case, this complex loses ammonia and carbon dioxide to produce the coordinatively unsaturated species $[\text{M}(\text{CO})_5]$, to whose unoccupied coordination site ammonia then adds (Scheme 1, path a). In the second case, elimination of CO_2 is accompanied by intramolecular rearrangement of the intermediate complex consisting of movement of the amino function to the metal atom (Scheme 1, path b), i.e., the formation of amine-substituted complex takes place by a four-centred mechanism.

To test both possibilities a special experiment was

carried out with the strongly coordinating PPh_3 being added to the reaction mixture. The reaction products were monitored by IR spectral changes. A single amino-substituted product appears to form even in the presence of excess PPh_3 , and this is revealed in the spectrum of the reaction mixture as the main strong $\text{C}=\text{O}$ stretching band at 1930 cm^{-1} (THF-ethanol 1:3 as a solvent).

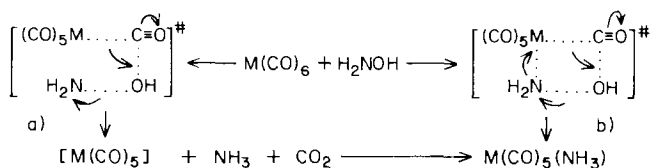
Additional support for such an assignment was provided when some preformed powdered $\text{W}(\text{CO})_5(\text{NH}_3)$ was placed in the reaction mixture. As a result, intensity of the initial absorption band increased without change of frequency. On the contrary, when $\text{W}(\text{CO})_5(\text{PPh}_3)$ was added in the same way, a new additional band appeared at 1942 cm^{-1} in the $\nu(\text{CO})$ region in agreement with literature data for this triphenylphosphine mono-substituted complex [8].

If the reaction mixture is allowed to stand for a few hours after the reaction with NH_2OH has completed, this band also appears in the spectrum and its intensity increases in time. In the preparative synthesis, when the concentration of reagents is an order of magnitude higher, it has been possible to detect the triphenylphosphine complex over 1.5–2 h. A similar result was observed for systems with hexacarbonyls of Mo and Cr. Thus it may be concluded that the phosphine-substituted compound is produced only as a result of NH_3 ligand replacement by PPh_3 in the initially formed

Table 2

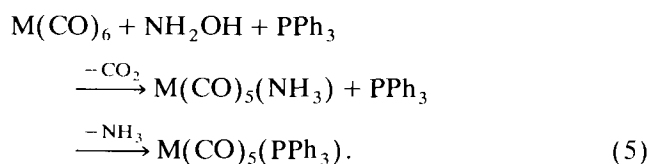
Rate constants and activation parameters for the reactions $\text{M}(\text{CO})_6 + \text{NH}_2\text{OH}$ in diglyme

M	$t^\circ\text{C}$	k_2 ($\text{l mol}^{-1}\cdot\text{s}^{-1}$)	E_a eff (kJ mol^{-1})	$\lg A_0$
Cr	19.4	0.217 ± 0.004	24.8 ± 1.4	4.4 ± 0.3
	22.3	0.243 ± 0.003		
	25.8	0.283 ± 0.005		
	27.3	0.290 ± 0.003		
	29.5	0.323 ± 0.002		
Mo	19.4	0.334 ± 0.004	26.8 ± 1.7	4.3 ± 0.3
	22.3	0.383 ± 0.007		
	25.8	0.426 ± 0.006		
	27.3	0.469 ± 0.008		
	29.5	0.477 ± 0.007		
W	10.4	0.283 ± 0.004	21.1 ± 1.5	3.3 ± 0.3
	20.5	0.392 ± 0.003		
	25.8	0.441 ± 0.010		
	30.5	0.523 ± 0.002		



Scheme 1.

amino-substituted carbonyl complex, and the overall reaction scheme is



(M = Cr, Mo, W)

In other words, PPh₃ does not take part in the first step of the reaction, and the amino complex is most probably formed by a four-centred intramolecular mechanism (Scheme 1, path b).

The alternative mechanism involving the coordinatively unsaturated species [M(CO)₅] was proposed earlier for the reaction of M(CO)₆ (M = Cr, Mo, W) assisted by Me₃NO [13]. This conclusion was based on IR spectral evidence of the rapid formation of M(CO)₄(PPh₃)₂ complexes during these processes. However, the analysis of the spectrum for the reaction mixture W(CO)₆ + Me₃NO + PPh₃ (unfortunately, IR stretching frequencies were not presented in ref. [13]) and its comparison with published spectral data for VIb metal phosphine-substituted carbonyl complexes have revealed that the absorption band at ca. 1920 cm⁻¹ of the single rapidly formed product is unlikely to arise from W(CO)₄(PPh₃)₂ or W(CO)₅(PPh₃). In fact, *trans*-W(CO)₄(PPh₃)₂ could be indicated by the strong ν(CO) vibration at ca. 1890 cm⁻¹ [15,16]) and the *cis*-isomer is expected to give rise to four strong bands in the range 1870–2020 cm⁻¹ [17,18]). As far as the W(CO)₅(PPh₃) complex is concerned a strong vibration band at ca. 1942 cm⁻¹ must be detectable in its spectrum [19,20]. Most likely the band at ca. 1920 cm⁻¹ corresponds to the trimethylamine mono substituted carbonyl complexes W(CO)₅(NMe₃) [15] which is one of the most probable reaction products.

To test what product actually forms in the reaction W(CO)₆ + Me₃NO + PPh₃ we have reproduced the conditions reported in [13]. After about 20% of the starting W(CO)₆ was reacted dry W(CO)₅(NMe₃) [15] was added and IR spectrum recorded. The intensity of the initially strongest ν(CO) band of the rapidly formed product increased, but the spectral position of this band was unchanged. On the contrary, when a portion of solid W(CO)₅(PPh₃) was added in a similar way, an additional band appeared at 1939 cm⁻¹. The same band attributed to compound W(CO)₅(PPh₃) was noted in the spectrum of the initial mixture when it had been allowed to stand for a day. That may be a result of NMe₃ replacement by PPh₃ in the initially formed complex W(CO)₅(NMe₃). Apparently, in the reaction M(CO)₆ (M = Cr, Mo, W) with Me₃NO, as in the reaction with NH₂OH, the monoaminopentacarbonyl complexes are initially formed possibly followed by

NMe₃ replacement by another n-donor reagent placed in the reaction mixture.

The above evidence, with consideration of the literature data [13], thus allow us to conclude that the interaction of Group VIb metal carbonyls with both hydroxylamine and trimethylaminoxide consists of nucleophilic attack of NH₂OH or ONMe₃ at the carbonyl carbon atom followed by the present CO group being oxidized to result in CO₂ elimination simultaneously with movement of the amino function to the metal atom.

3. Experimental section

3.1. Reagents

Metal carbonyls were purified by recrystallization from dichloromethane before use. Solvents were purified and dried by published procedures [22]. NH₂OH was prepared by the literature method [23], by thermal decomposition of NH₂OH · 1/3 · H₃PO₄ in vacuo followed by recrystallization of distilled product from dry ethyl alcohol. PPh₃ was purified by the neutralization of PPh₃ · HCl, precipitated from aqueous hydrochloric acid, with aqueous NH₃ followed by the recrystallization of crude product from diethyl ether and then three times from ethanol.

3.2. Instrumentation

Infrared spectra were recorded on Specord IR-75 and Specord M-80 spectrometers with 0.2 mm CaF₂ cells. Ultraviolet-visible measurements were obtained on a Specord UV-Vis spectrometer using 10 mm quartz cells.

3.3. Kinetic measurements

Rate data for the disappearance of reactant metal complexes were obtained by monitoring UV-Vis spectral changes (fixed wavelength was about 290 nm). Reaction products were studied by monitoring IR spectral changes in the ν(CO) region. All the reactions were performed under pseudo-first-order conditions with the concentration of NH₂OH at least 50 times greater than that of M(CO)₆ (ca. 10⁻⁴ M).

In a typical experiment with the UV-Vis spectrometer a cell containing a solution of M(CO)₆ in diglyme was placed in a temperature-regulated jacket. This jacket and the flask containing a solution of NH₂OH in diglyme were held for 30 min at constant temperature (controlled to within ±0.1°) in a thermostat bath. A solution of NH₂OH was then removed by syringe and the resultant spectral changes were monitored with time.

3.4. Syntheses

All the reactions were performed under an argon atmosphere unless otherwise specified. The spectral data are listed in Table 1.

3.4.1. $(\mu\text{-H})\text{Os}_3\{\mu\text{-OCNHCH}_2\text{CO(O)Et}\}(\text{CO})_9\{\text{NH}_2\text{-CH}(\text{CH}_3)\text{CO(O)Et}\}$ (**IIa** and **IIb**)

Hydrogen peroxide ($5 \cdot 10^{-3}$ mol) in form of a solution (0.25 ml) of aqueous 30% H_2O_2 in THF (1:4 by volume) and L- $\text{NH}_2\text{CH}(\text{CH}_3)\text{CO(O)Et}$ (0.5 ml, $4.2 \cdot 10^{-3}$ mol) were added to $(\mu\text{-H})\text{Os}_3\{\mu\text{-OCNHCH}_2\text{CO(O)Et}\}(\text{CO})_{10}$ (**I**) (200 mg, $2.04 \cdot 10^{-4}$ mol) in THF (30 ml) and allowed to stand for 2.5 h at ambient temperature. The reaction mixture was then chromatographed on a thin-layer silica plate in benzene-hexane-diethyl ether (7:7:4) as eluent to give three bands. The first proved to be unreacted **I**. Bands 2 and 3 were identified later as geometrical isomers **a** and **b** of complex **II**, respectively, and each was eluted with diethyl ether. After evaporation to dryness of solvent from the filtered eluates, **IIa** (60 mg, 27.5%) and **IIb** (49 mg, 22%) were obtained along with the return of **I** (93 mg, 46.5%). The yields of **IIa** and **IIb** were 51% and 42% respectively (based on reacted **I** only).

Yields of isomers **IIa** and **IIb** were variable and dependent on the reaction time due to isomerization between **a** and **b**. A very long reaction time led to trace amounts of **IIa** and the starting **I** with an increase in the amounts of **IIb** and of decomposition products (i.e., a brown uncharacterizable tar). Both **IIa** and **IIb** were presented as two diastereomers (**IIa1**, **IIa2** and **IIb1**, **IIb2**).

Attempts at resolution of **IIb** into diastereomers were unsuccessful. Multiple development of the chromatography plates (20 × 20 cm) was necessary to separate diastereomers **IIa1** and **IIa2**. In this case, **IIa** (52 mg) was chromatographed repeatedly in hexane-diethyl ether (5:7) as eluent. The two bands were eluted with diethyl ether. Addition of pentane to filtered eluates followed by slow rotary evaporation gave 17.5 mg (34%) of **IIa1** and 14.5 mg (28%) of **IIa2** along with some isomerization product (**IIb**) plus decomposition products on the starting line of the chromatogram. For **IIb** found: Os 53.30, C 21.20, H 1.87; $\text{Os}_3\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_{14}$ calcd.: Os 53.30, C 20.45, H 1.72%. It should be noted that the ^1H NMR spectra of both **IIa1** and **IIa2** contained some additional resonances of **IIb** of low intensity, which are not shown in Table 1.

3.4.2. $(\mu\text{-H})\text{Os}_3\{\mu\text{-OCNHCH}_2\text{CO(O)Et}\}(\text{CO})_9\{\text{NH}_2\text{-CH}_2\text{CO(O)Et}\}$ (**IIIa** and **IIIb**)

To the stirred solution of **I** (36 mg, $3.45 \cdot 10^{-5}$ mol) in THF (1.5 ml) $\text{NH}_2\text{CH}_2\text{CO(O)Et}$ (0.03 ml, $3 \cdot 10^{-4}$ mol) and H_2O_2 ($3.17 \cdot 10^{-4}$ mol, 0.35 ml of a solution

of aqueous 30% hydrogen peroxide in THF, 1:10 by volume) was added. The solution was stirred for 2.5 h at room temperature and then passed through a silica gel plate using mixture benzene-hexane-diethyl ether (7:7:4) as eluent. Two geometrical isomers **IIIa** (with the larger R_f value) and **IIIb** were isolated as yellow powders in yields of 34% (9.5 mg) and 43% (11.9 mg) respectively. Some unreacted **I** (5 mg, 14%) was returned. For **IIIa** found: Os 53.90, C 20.29, H 1.60; $\text{Os}_3\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_{14}$ calcd.: Os 53.99, C 20.45, H 1.72%; ^{13}C NMR and X-ray diffraction studies for **IIIb** were described in [7].

3.4.3. $(\mu\text{-H})\text{Os}_3\{\mu\text{-OCNHCH}_2\text{CO(O)Et}\}(\text{CO})_9\{\text{NH}_2\text{-(CH}_2)_4\text{CH}_3\}$ (**IVb**)

A mixture of **I** (60 mg, $6 \cdot 10^{-5}$ mol), amylamine (34.8 mg, $4 \cdot 10^{-8}$ mol) and H_2O_2 ($4 \cdot 10^{-4}$ mol in the form of 0.44 ml of a 0.9 M solution in THF) in THF (3 ml) was held at room temperature for 15 min. Chromatography on thin-layer silica plates using hexane-diethyl ether (5:7) as eluent showed firstly two bands which were believed to be geometrical isomers **a** and **b**. Because of the rapid isomerization of **a** into **b** the bands merged smoothly together. The elution of the resulting band with diethyl ether and evaporation of solvent afforded a yellow-orange powder identified by mass spectrometry and IR spectroscopy as isomer **b** of $(\mu\text{-H})\text{Os}_3\{\mu\text{-OCNHCH}_2\text{CO(O)Et}\}(\text{CO})_9\{\text{NH}_2(\text{CH}_2)_4\text{CH}_3\}$ (**IVb**; 45.5 mg, 73%).

3.4.4. $(\mu\text{-H})\text{Os}_3\{\mu\text{-OCNHCH}_2\text{CO(O)Et}\}(\text{CO})_9(\text{NH}_3)$ (**Va** and **Vb**)

a) Complex **I** (39.2 mg, $4 \cdot 10^{-5}$ mol) and NH_2OH (15 mg, $4.5 \cdot 10^{-4}$ mol) were dissolved in THF (2 ml) followed immediately by filtration of the reaction mixture through silica in order to remove any excess NH_2OH and to reduce decomposition. The rest of the products were eluted from silica with diethyl ether. The resulting solution was concentrated to 2–3 ml and chromatographed on a thin-layer silica plates with hexane-diethyl ether (5:7) as eluent affording three fractions. A weak band (1) which was unreacted complex **I** and two extended bands (2 and 3) were observed to each other. The isomers were eluted with diethyl ether. Evaporation of the solvents afforded the yellow powders **Va** (7 mg, 18%) and **Vb** (12 mg, 31%).

b) Through a mixture of **I** (120 mg, $1.2 \cdot 10^{-4}$ mol) and H_2O_2 ($1.3 \cdot 10^{-3}$ mol in the form of 0.36 ml of solution of aqueous 30% hydrogen peroxide in THF, 1:10 by volume) in THF (8 ml), NH_3 mixed with argon was passed slowly with stirring. After 5 min the reaction mixture was chromatographed on thin-layer silica plates using hexane-diethyl ether (5:7) as eluent. Two bands of products were eluted with diethyl ether. Isomers **Va** (28 mg, 24%) and **Vb** (48 mg, 40%) were obtained. For **Vb** found: Os 58.62, C 17.55, H 1.20; $\text{Os}_3\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_{12}$ calcd.: Os 58.79, C 17.31, H 1.24%.

3.4.5. $(\mu\text{-H})\text{Os}_3\{\mu\text{-OCNHCH}_2\text{CO(O)Et}\}(\text{CO})_9(\text{NH}_2\text{-CH}_3)$ (**Vib**)

Complex **I** (137 mg, $1.4 \cdot 10^{-4}$ mol) was dissolved in THF (5 ml) and CH_3NHOH ($4.79 \cdot 10^{-4}$ mol as 12.5 ml of 0.38 M ethanolic solution) was added. The mixture was allowed to stand for 1 h at ambient temperature and then chromatographed on a thin-layer silica plate using hexane-diethyl ether (5:7) as eluent. Two fractions of products were eluted with diethyl ether. Fraction 2 was shown to be the isomer **Vib** (70 mg, 51%). The fraction 1 was suggested to be isomer **a** which was unstable and isomerized into **b** with decomposition during the isolation. For **Vib** found: Os 58.00, C 18.34, H 1.43; $\text{Os}_3\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_{12}$ calcd.: Os 57.95, C 18.28, H 1.42%.

3.4.6. $(\mu\text{-H})\text{Os}_3\{\mu\text{-OCNHCH}_2\text{CO(O)Et}\}(\text{CO})_9\{\text{NH}(\text{C}_2\text{H}_5)_2\}$ (**VIIa and VIIb**)

Hydrogen peroxide ($2 \cdot 10^{-4}$ mol in form of 0.22 ml of a solution of aqueous 30% H_2O_2 in THF, 1:10 by volume) was added to the mixture of **I** (45.6 mg, $4.6 \cdot 10^{-5}$ mol) and $(\text{C}_2\text{H}_5)_2\text{NH}$ (0.02 ml, $1.9 \cdot 10^{-4}$ mol) in diethyl ether (3 ml). The solution was allowed to stand for 4 h at ambient temperature and then chromatographed on a thin-layer silica plate using benzene-hexane-diethyl ether (7:7:4) as eluent. Two bands of products were observed. Band 1 was shown to be unreacted **I** (4.7 mg, 10%). Bands 2 and 3 were identified as the isomers **VIIa** (18.4 mg, 39%) and **VIIb** (16.5 mg, 35%), respectively.

3.4.7. $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$

$\text{Os}_3(\text{CO})_{12}$ (40 mg, $4.4 \cdot 10^{-5}$ mol) was dissolved in the mixture of THF (8 ml) and CH_3CN (2 ml). NH_2OH (28 mg, $8.4 \cdot 10^{-4}$ mol) was then added. The solution was allowed to stand for 15 min and then passed through silica to remove excess NH_2OH and to reduce decomposition to a minimum. The resulting solution was concentrated until a yellow solid began to precipitate and was then cooled to -10°C . The precipitated yellow $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ was washed with pentane and dried under vacuum (32.7 mg, 81%). The values of R_f from TLC and IR data (in CH_2Cl_2) were essentially the same as those resulting from other preparations [14].

3.4.8. $\text{M}(\text{CO})_5(\text{NH}_3)$

A weighed portion of $\text{M}(\text{CO})_6$ ($\sim 1 \cdot 10^{-3}$ mol) was dissolved in THF. The mixture was stirred briefly during the addition of an alcohol solution of either equimolar quantity or any excess of NH_2OH . The reaction mixture was held at room temperature until only trace amounts of starting material were observed on TLC (hexane-diethyl ether 1:1 as eluent). The solution was evaporated by rotary distillation to a moist

Table 3

Preparation of the compounds $\text{M}(\text{CO})_5(\text{NH}_3)$ (M = Cr, Mo, W)

M	React. time (min)	M.p. ($^\circ\text{C}$)	Yield (%)	Analysis (%) (found/calcd.)	IR-spectra, $\nu(\text{CO})$, cm^{-1}
Cr	20–30	150 (dec.)	82	M: 24.8/24.9 C: 28.66/28.71 H: 1.84/1.44 N: 6.60/6.69	1915w, 1936m, 2065vs (in cyclohexane)
Mo	60–90	100 (dec.)	59	M: 37.47/37.94 C: 23.57/23.71 H: 1.20/1.19 N: 5.53/5.55	1920w, 1943m, 2074vs (in hexane)
W	40–45	150 (dec.)	74	M: 53.96/53.96 C: 17.53/17.59 H: 0.77/0.88 N: 3.65/4.11	1920w, 1934m, 2074vs (in hexane)

solid followed by an extraction with diethyl ether or dichloromethane. The extract was cooled in a NaCl-ice bath to precipitate crystalline colourless unreacted $\text{M}(\text{CO})_6$ which was then filtered off. The yellow (or green-yellow) solid was produced by addition of cooled pentane to the filtered extract. The filtered and dried product was identified as $\text{M}(\text{CO})_5(\text{NH}_3)$. The specific experimental data are listed in Table 3.

References

- [1] J. Wender and P.N.Y. Pino, *Organometallic Syntheses*, Vol. 2, Wiley, 1977.
- [2] W. Hieber and A. Lipp, *Chem. Ber.*, 92 (1959) 2075.
- [3] H. Alper and J.T. Edwards, *Can. J. Chem.*, 48 (1970) 1543.
- [4] Tun-Yau Luh, *Coord. Chem. Rev.*, 60 (1984) 255.
- [5] M.O. Albers and N.J. Coville, *Coord. Chem. Rev.*, 53 (1984) 227.
- [6] V.A. Maksakov, V.A. Ershova, V.P. Kirin, I.F. Golovaneva, A.Ya. Mikhailova and A.P. Klyagina, *Dokl. Akad. Nauk SSSR*, 299 (1988) 1142.
- [7] V.A. Maksakov, V.A. Ershova, A.V. Virovets, Yu.L. Slovokhotov, N.V. Podberezhskaya and Yu.T. Struchkov, *Metalloorg. Khimia*, 4 (1991) 305.
- [8] E.J. Ditzel, B.F.G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, (1987) 1293.
- [9] V.A. Maksakov, V.A. Ershova, A.V. Virovets, N.V. Podberezhskaya, P.P. Semyannikov and A.G. Buyanovskaya, *Metalloorg. Khimia*, 6 (1993) 231.
- [10] B.F.G. Johnson, J. Lewis and D.A. Pippard, *J. Chem. Soc., Dalton Trans.*, (1981) 407.
- [11] V.A. Maksakov and V.A. Ershova, *Bull. Izobret. N 26* (1991) 87.
- [12] J.A. Smiga and W.L. Gladfelter, *Inorg. Chem.*, 25 (1986) 2667.
- [13] Y.-L. Shi, Y.-C. Gao, Q.-L. Shi, D.L. Kerstner and F. Basolo, *Organometallics*, 6 (1987) 1528.
- [14] Shen J.-K., Y.-L. Shi, Y.-C. Gao, Q.-L. Shi and F. Basolo, *J. Amer. Chem. Soc.*, 110 (1988) 2414.
- [15] U. Koelle, *J. Organomet. Chem.*, 133 (1977) 53.
- [16] W. Hieber and J. Peterhans, *Z. Naturforsch.*, 14b (1959) 462.
- [17] G. Shwenzer, M.Y. Darensbourg and D.J. Darensbourg, *Inorg. Chem.*, 11 (1972) 1967.
- [18] J. Chatt and H.R. Watson, *J. Chem. Soc.*, (1961) 4980.

- [19] F.A. Cotton and F.A. Kraihanzel, *J. Amer. Chem. Soc.*, 84 (1962) 4432.
- [20] S.O. Grim, D.A. Wheatland and W. McFarlane, *J. Amer. Chem. Soc.*, 89 (1967) 5573.
- [21] T.A. Magee, C.N. Matthews, T.S. Wang and J.M. Wotiz, *J. Amer. Chem. Soc.*, 83 (1961) 3200.
- [22] A.J. Gordon and R.A. Ford, *The Chemist's Companion*, Wiley, New York, 1972, p. 447.
- [23] G. Brauer (Ed.), *Handbuch der Präparative Anorganischen Chemie*, Stuttgart, 1975, p. 506.