Tetracarboxylatodirhenium Complexes Linked by Axial Cyano Bridges to Metalpentacarbonyl Ligands − Synthesis and Characterization

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Reaction of $Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4Cl_2$ with $[(CO)_5M–CN]Na$ (M = Cr, Mo, W) leads to tetranuclear complexes of formula $Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4[–NC–M(CO)_5]_2$ (M = Cr, Mo, W). These complexes were characterized by ^{1}H-, ^{13}C-, and ^{95}Mo-NMR, IR and Raman spectroscopy, elemental analysis and examined by cyclic voltammetry. The applied methods show the donor capabilities of the $[(CO)_5M–CN]^-$ ligands which shift electron density towards the Re centers weakening the Re–Re quadruple bond. The Re–Re bond lengths and the ν(Re–Re) force constants are estimated based on the FT-IR and Raman examinations. Photochemical examinations and TG/MS experiments have also been conducted. The latter method shows that the product complexes decompose around 100 °C, by first loosing their carbonyl substituents; as do the Cr, Mo, W precursor compounds. The dirhenium tetrapivalate unit decomposes only at higher temperatures in a distinct second step.

Introduction

Dirhenium carboxylates of the general formula $Re_2(\mu\text{-}O_2CR)_4X_2$ were among the first molecules containing metal−metal quadruple bonds to be correctly described.[1] Their recognition followed closely upon the heels of the structural characterization of the $[Re_2Cl_8]^{2-}$ anion and the correct treatment of its bonding.[2] However, the first reports of rhenium carboxylates appeared before this, but failed to take into account the possibility of metal−metal bonding.[3] In the interim a very extensive chemistry of $Re_2(\mu\text{-}O_2CR)_4X_2$ complexes has been developed.[1] Nevertheless, the variation of the ligands in axial position (X) remained rather limited. In particular, halides and pseudohalides, e.g. Cl, Br, I, NCS etc. have been reported.[4] Ligands containing transition metals are rare. To our knowledge, only one such compound with perrhenate as axial ligand has been structurally characterized.[4c] During the course of our own work on mixed transition metal complexes linked by nitrile and cyano groups[5] we came to examine the reactivity of $Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4Cl_2$ with $[(CO)_5M−CN]Na$ (M = Cr, Mo, W). The latter complexes have gained considerable interest in recent times due to their ability to form cyano bridges to other molecules.[6] The results of these reactions and the characterization of the products are reported in this work.

Results and Discussion

Synthesis and Spectroscopic Characterization

Mixing of a suspension of dichlorodirhenium tetrapivalate (**1**) with $[(CO)_5M−CN]Na$ [M = Cr (**2**) , Mo (**3**), W (**4**)] in THF at room temperature leads to a color change from brown to very dark red. A white precipitate is formed. According to Scheme 1, molecules of composition $Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4[−NC−M(CO)_5]_2$ [M = Cr (**5**), Mo (**6**), W (**7**)] and sodium chloride as stoichiometric byproduct are formed. After extraction with dichloromethane to remove the NaCl, the compounds **5**−**7** can be precipitated by the addition of *n*-pentane. The yields of isolated compounds obtained in this way are nearly quantitative. Compounds **5**−**7** can be handled in air at room temperature.

As it might be expected, the ^{1}H-NMR spectra are not very informative. Both complex **1** and complexes **5**−**7** display a singlet at $\delta(^1H) = 1.52$. The ^{13}C-NMR spectra clearly indicate the formation of the complexes **5**−**7**. The ^{13}C-NMR data are summarized in Table 1. All signals are influenced by the coordination. The strongest shift difference can be seen in the signal corresponding to the carbon atom of the bridging cyano group. This signal is shifted ca. 15−25 ppm to higher field, depending on the central metal atom of the coordinating axial ligand. Interestingly, the shifts of the corresponding signals are very similar in all product molecules in remarkable contrast to the Cr, Mo, W

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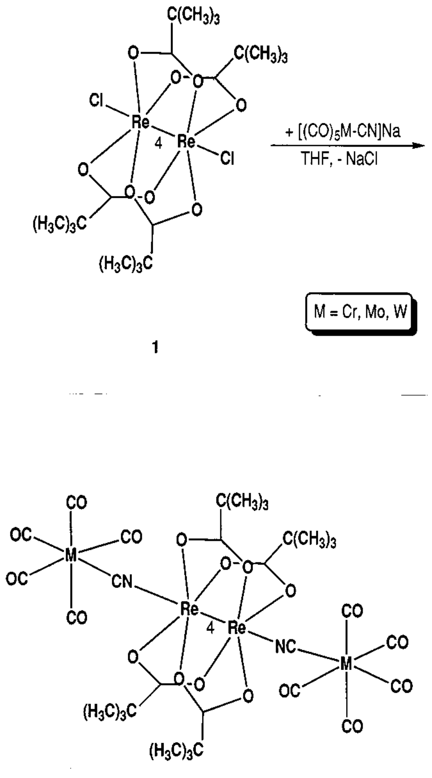

1

5-7

Scheme 1

Table 2. ^{95}Mo-NMR data for $Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4[-NC-Mo(CO)_5]_2$ (**6**, in CD_2Cl_2) and $[(CO)_5Mo-CN]Na$ (**2**, in CD_3OD)

Temp. [°C]	δ(^{95}Mo) [ppm]	$\Delta\nu_{1/2}$ [Hz]
	$[(CO)_5Mo-CN]Na$	
−25	−1892	190
+25	−1882	130
+60	−1875	190
	$Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4[-NC-Mo(CO)_5]_2$	
−85	−1580	5000
−40	−1610	5300
±0	−1620	5900
+25	−1690	6300
+35	−1700	6700

precursor compounds. The carboxylate carbon atoms are nearly uninfluenced by the coordination, the ^{13}C signals of the carbonyl C atoms are only slightly (ca. 5 ppm) shifted upfield. The influence of the coordination is also clearly reflected in the ^{95}Mo-NMR spectrum of compound **6** when compared with that of compound **3**. The signal is shifted more then 270 ppm to lower field and is significantly broadened (ca. 130 Hz in the starting material **3**, more than 5000 Hz in compound **6**). The ^{95}Mo-NMR data also display a temperature dependence as depicted in Table 2. A temperature decrease of 100°C causes a downfield shift of ca. 100 ppm in the complex **6**. This seems to be due to the somewhat reduced electron-transfer capability of the complexes at elevated temperatures, probably due to an increase of the thermal movements of the ligands. The latter is reflected in the significantly increasing half widths of the ^{95}Mo-NMR signals at higher temperatures. As can be also concluded from the ^{13}C NMR the electron density in compound **6** is withdrawn from the Mo core. The axial Cr, Mo, W ligands therefore act as donors, which is in good agreement with the expectations and earlier examinations of the behavior of the $[(CO)_5M-CN]^-$ moiety.[6]

IR and Raman Spectroscopy

The characteristic IR and Raman bands of the complexes **2**−**7** are summarized in Table 3. The vibrational symmetry of the complexes **5**−**7** is D_{4h} which leads to the alternativity of the IR and Raman bands especially for the skeletal modes involving displacements of the Re atoms. The infrared spectra of the starting pentacarbonylmetal complexes **2**−**4** are also tabulated for a better understanding of the vibrational assignment. According to theoretical considerations of the vibrations, the very characteristic and important stretching modes of the linear CN−ReRe−NC moiety has no interaction with the ReO vibrations which involve displacements perpendicular to the linear molecular axis. According to the selection rules the Re−Re and the inphase symmetric stretchings of the Re−N and C−N are Raman-active and the antisymmetric contribution of Re−N and C−N stretches are IR-active. Since the vibrational interactions via the heavy Re atoms should be very weak, the IR and Raman stretching frequencies are expected to be rather close to each other. Because of the above-mentioned very weak or negligible vibrational coupling through Re−Re groups, the assignment of the $[NC-M(CO)_5]^-$ moieties can be performed on the basis of C_{4v} local symmetry (see Table 3). The general features reflected by the experimental observations can be summarized as follows:

The IR data of the complexes **5**−**7** show that the ν(CO) vibrations are shifted to higher wavenumbers relative to the starting materials **2**−**4**. However, in both types of complexes the carbonyl−metal bond is dominated by the back donation of the metal core to the carbonyl groups. The

Table 1. ^{13}C-NMR data of complexes **1**−**7** [ppm]

	1 ($NCCD_3$)	**2** ($NCCD_3$)	**3** ($NCCD_3$)	**4** ($NCCD_3$)	**5** (CD_2Cl_2)	**6** (CD_2Cl_2)	**7** (CD_2Cl_2)
$C(CH_3)_3$	29.3	−	−	−	27.5	27.4	27.4
$C(CH_3)_3$	42.8	−	−	−	41.1	41.2	41.1
NCMCO	−	221.5	211.1	206.0	217.9	207.9	201.0
OCMCO	−	218.5	206.8	201.4	215.5	204.4	195.2
OC(R)O	207.3	−	−	−	205.6	205.7	200.5
NC	−	153.8	149.2	140.0	124.6	124.3	124.7

back-donating effect to the π* orbitals of the carbonyl groups is decreased in the product molecules because part of the electron density at the metal centers is now shifted towards the CN units.[7] Accordingly, the ν(CN) vibrations are shifted ca. 10−20 cm^{-1} to lower wavenumbers. Electron density is withdrawn from the C≡N bond to the rhenium atoms.

The vibrational frequencies of the $Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4$ unit are only slightly influenced by the new metalpentacarbonyl ligands. Characteristic bands were observed at 1550 (w), 1430 (s) and 1220 (vs) cm^{-1}, referring to one asymmetric and two symmetric COO stretching vibrations, respectively. The COO deformational mode is observed as a strong IR band at 630 cm^{-1}. The ReO stretching modes appear in the range of 360−480 cm^{-1} assigned to a_{1g}, e_u, a_{2u} and e_g species (see Table 3).

The very strong Raman bands at 275, 277 and 288 cm^{-1} can unambiguously be assigned to stretching frequencies of the quadruple bond between the rhenium atoms for the complexes **5−7**. The position and intensity of this Raman bands[8] suggests that coupling occurs between the metal−metal stretching mode and the rhenium−cyanide stretching mode. The Re−Re stretching vibraton of these complexes are shifted to higher energies relative to that of $Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4Cl_2$ (**1**) in accord with the occurrence of less ReRe→(N≡CR) π back-bonding. We can observe a slight strengthening of the Re−Re bond in the Re-Re←N≡CM(CO)$_5$ moiety in the order M = Cr < Mo < W.

Simplified force-constant calculations have been performed using the linear CN−ReRe−NC moiety of the complexes. On the basis of literature values of bond lengths and Re−Re stretching frequencies the metal−metal stretching force constants have been calculated for the compounds shown in Table 4. A clear correlation has been observed between bond lengths and force constants. This relation can be used to predict bond lengths for the newly synthesized complexes **5−7**. As the Re−Re force constants are increasing from 4.15 to 4.55 Ncm^{-1}, consequently the predicted bond lengths are shortened from 226 to 223.6 pm for complexes **5−7** (see Table 4).

Electrochemical Studies

Complexes **5−7** have a chain of 12 atoms along the Re−Re axis, with four triple bonds (2 C≡O and 2 C≡N) and one quadruple Re−Re bond which will show some degree of conjugation due to π back-donation. Cyclovoltammetric studies have shown that both the organometallic ligands $[(CO)_5M{-}CN]^-$, and the $Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4X_2$ moiety are electrochemically active. The former undergo 1-e^- oxidations which are only reversible for M = Cr.[9a] The latter undergo 1-e^- reduction to give the paramagnetic anions $[Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4X_2]^-$ possessing a $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$ electronic configuration.[9b] These facts suggested the possibility of obtaining interesting redox activities for such complexes and, therefore, an electrochemical survey was carried out. The cyclic voltammograms (CV) of the tetranuclear complexes **5−7** were measured in a CH_2Cl_2 solution in the presence of $N[CC(CH_3)_3]_4BF_4$ as supporting electrolyte and the data are presented in Table 5. For sake of comparison, the same table presents the data collected for the organometallic ligands **2−4**. These could not be obtained in the same solvent due to insolubility and were, therefore, measured in $NCCH_3$ in good agreement with reported values.[9a] The values obtained under our conditions for complex **1** in CH_2Cl_2 are also in agreement with those reported in ref.[9b]

The voltammograms of **6** and **7** are essentially similar. They only present a totally irreversible oxidation wave at $E_{pa} \approx 1.15$ V without any cathodic response. In the case of **5**, this wave is better defined and a small cathodic response at $E_{pa} = 0.82$ V is already present, as depicted in Figure 1. A second irreversible oxidation in the CV of **5** is indicated by the anodic peak at $E_{pa} = 1.39$ V. Lowering of the temperature to −50°C increases the reversibility of the former wave ($i_a/i_c \approx 1$) suggesting that its lack of reversibility at room temperature results from a chemical decomposition process taking place after oxidation. In agreement, the anodic peak at $E_{pa} = 1.39$ V disappears completely at −50°C. No wave was present in the region expected for the oxidation of free, uncoordinated ligands $[(CO_5)M{-}CN]^-$ which attests to the stability of the adducts **5−7**.

In complex systems like these tetranuclear species it is obviously difficult to assign the part of the molecule whereupon the oxidation is based. However, we assign these oxidations to the $[(CO_5)M{-}CN]$ center (M = Cr, Mo, W), in the case of the Cr derivative **5** ($E_{pa} = 1.15$ V) this corresponds to a shift of the E_{pa} signal to more positive potentials by ca. 0.3 V since the anion **2** undergoes a reversible oxidation in that region at $E_{pa} = 0.73$ in $NCCH_3$. The irreversible anodic waves of **3** and **4** also undergo a similar shift towards higher potentials in their corresponding complexes **6** and **7**. In this case a more accurate comparison of potentials is not possible because of the insolubility of the complexes **2−4** are in CH_2Cl_2. Although the lack of reversibility does not allow an accurate interpretation, these results suggest that the organometallic ligands $[M(CO)_5{-}CN]^-$ (**2−4**) donate electronic density to the ReRe core, therefore becoming more difficult to be oxidized.

As we mentioned above, the complexes $Re_2\{O_2CC(CH_3)_3)\}_4X_2$ undergo a 1-e^- reduction to their monoanions. This reduction presents a linear dependence on the nature of the halogen X, being more difficult in the case of X = Cl relative to X = I by only 0.1 V.[9b] In view of the reversible voltammetric behavior of these halides and the ready acceptance of an anti-bonding electron by the Re−Re quadruple bond molecular orbital framework, the absence of a corresponding reduction wave in all three complexes **5−7** is quite surprising. All experimental modifications attempted (lowering the temperature to −70°C, changing the sweep rate, increasing the sample concentration) failed to reveal any reduction wave. At present we cannot offer a sound explanation for the absence of this reduction although it may be considered consistent with a significant electron transfer from the axial ligands capable of modifying the

Table 3. Selected characteristic vibrational frequencies [cm^{-1}] for complexes **2−7**

5		**2**	**6**		**3**	**7**		**4**	assignments
IR	Raman	IR	IR	Raman	IR	IR	Raman	IR	
2976 w			2976 w			2974 w			CH_3 asym str
			2936 vw			2938 vw			CH_3 asym str
			2906 vw			2906 vw			CH_3 sym str
2101 m			2101 m			2105 m			CN str [a_{2u}][a]
		2111 m			2099 s			2099 w	CN str [a_{1g}]
		2054 w			2066 m			2058 m	CO sym str (a_1)[b]
2041 vs		1996 s	2038 s		1986 s	2029 s		1983 s	CO asym str (b_1)
1931 vs		1911 vs	1933 vs		1921 vs	1929 vs		1908 vs	CO asym str (e)
		1826 s			1846 s			1815 sh	CO sym str (a_1)
1221 vs			1219 vs			1221 vs			COO sym str [e_u]
	630 vw			630 w			630 w		COO bend [a_{1g}]
627 m			629 s			627 s			COO bend [e_u]
679 m	665 w	683 m	606 s	600 w	612 m	594 s		600 m	M−CO bend (a_1)
660 vs	650 w	654 vs	590 vs		591 vs	581 s	580 w	581 s	M−CO bend (e)
		550 w			533 w			541 w	M−CO bend (e)
		474 m							
	480 m			470 w			460 m		Re−O str. [a_{1g}]
			468 m			464 m			Re−O str [e_u]
	445 m	450 m	450 m	450 w	435 w		435 m	444 w	M−CO str (e)
	384 s			411 m			435 m		M−CO str (a_1)
390 s			375 s			377 vs			Re−O str [a_{2u}]
	(384 s)			360 w			386 w		Re−O str [e_g],
346 w				345 w			334 w		M−CN str. (a_1)
330 w				330 w			312 w		M−CN bend (e)
	275 s			277 s			288 s		ReRe str [a_{1g}]
243 w			237 w			235 w			Re−CN str (a_{2u})
	225 w,b			230 w,b			245 w,b		Re−CN str (a_{1g})
185 sh			187 m			184 m			ReReN bend [e_u]
	175 sh			175 sh			200 sh		ReReN bend [e_g]
173 m			170 m			168 m			CMC bend (?)[c]

[a] In square brackets are the predicted symmetry species are included referring to D_{4h} general (idealized) point group of the whole molecule. − [b] In round brackets are the suggested symmetry species due to C_{4v} local symmetry of the metalpentacarbonyl moiety. − [c] The C−M−C bond-angle deformation modes are strongly overlapping vibrations and can be attributed to all IR-active species (a1 and e) of the metalpentacarbonyl fragment.

Table 4. Bond lengths [pm], stretching frequencies ν [cm^{-1}] and force constants K [10^2 Nm^{-1}] of selected complexes with Re−Re quadruple bonds

compound and reference	Re−Re bond lengths	ν(M−M)	K(M−M)[b]
$Re_2OCl_5(O_2CCH_2CH_3)_2 \cdot (PPh_3)_2$[8b]	252.0	216	2.559
Re_2Cl_5(2,5-dithiahexane)[8b]	229.0	267	3.011
$Re_2(O_2CCH_3)_4Cl_2$[8b,8c]	223.6(1)	288	4.550
$[Re_2F_8][NBu_4] \cdot 2\ Et_2O$[8d,8e,8f]	218.8(3)	318	5.547
1	223.6(1)	288	4.550
5	226.0[a]	275	4.149
6	225.5[a]	277	4.202
7	223.5[a]	288	4.550

[a] Estimated bond lengths (see text): occuracy ca. 0.5 pm. − [b] The simplified calculation gives overestimated values.

electronic framework of the Re−Re bond to such an extent as to shift the reduction potential to the outside of the solvent window. A more detailed study of the electrochemical behavior of axially substituted ReRe complexes of type $[Re_2\{\mu\text{-}O_2CC(CH_3)_3)\}_4L_2]^{n+}$ as well as a theoretical investigation of the orbital interactions in complexes **5−7** is currently under way. Preliminary results show that the analogous nitrile complexes $[Re_2\{\mu\text{-}O_2CC(CH_3)_3)\}_4(NCR)_2]^{2+}$ (R = Me, Ph) undergo irreversible reductions in the expected region, ca. $E_{pa} \approx -0.5$ V.

Thermogravimetry and Thermal Decomposition

The Re precursor compound **1** is thermally very stable, subliming at ca. 380°C (onset temperature) leaving a residue of only 3.6%. Possibly only those parts of the compound decompose which cannot sublime quickly enough. Lowering the amount of compound in the crucible also lowers the amount of the remaining residue. The mass spectrometer we used, which is able to detect only masses of $m/z < 400$, does not record any species.

The Mo precursor **3**, of which the thermal decomposition behavior was examined, starts to decompose quickly at ca. 160°C (onset 158.3°C). Carbonyl ligands can be detected as volatile fragments in the mass spectrometer. Only traces of $[Mo(CO)_6]^+$ (m/z = 264) have been detected. This molecule has also been detected during the thermal decomposition of related complexes.[6e] The remaining residue contains 54.6% of the original mass of the compound. Thus, 45.4% of the sample mass is lost during the heating process. This is in good agreement with the total mass of CO in the starting material (48.8%).

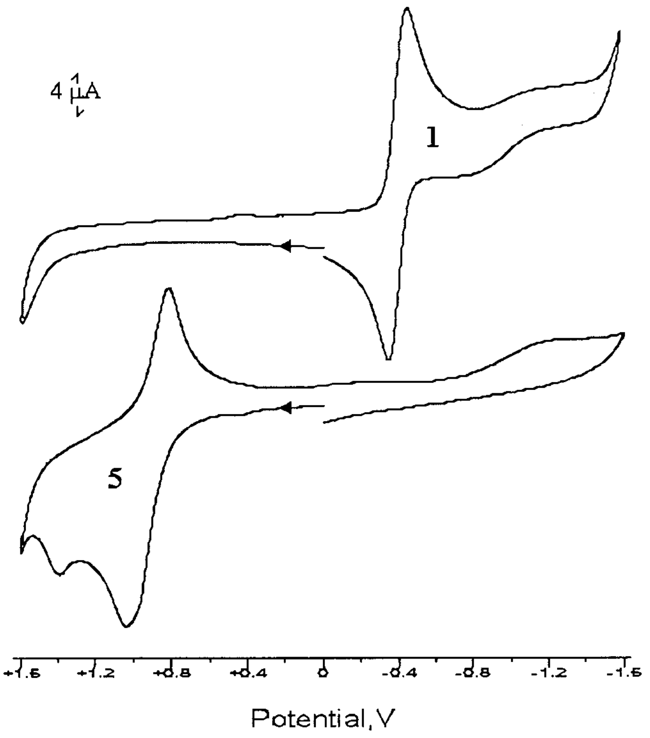

Figure 1. Cyclic voltammogram of $Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4Cl_2$ (**1**) and $Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4[-NC-Cr(CO)_5]_2$ (**5**)

Table 5. Cyclovoltammetric data (recorded in CH_2Cl_2)

compound		E_{pa} [V][a]	E_{pc} [V][b]	comment
$Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4Cl_2$	**1**	−0.35	−0.45	reversible
$[(CO)_5Cr-CN]Na$	**2**	0.73[c]	0.65[c]	reversible
$[(CO)_5Mo-CN]Na$	**3**	0.85[c]	–	irreversible
$[(CO)_5W-CN]Na$	**4**	0.82[c]	–	all irreversible
		1.11[c]	–	
$Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4$-$[-NC-Cr(CO)_5]_2$	**5**	1.03	0.82	all irreversible
		1.39	–	
$Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4$-$[-NC-Mo(CO)_5]_2$	**6**	1.14	–	irreversible
$Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4$-$[-NC-W(CO)_5]_2$	**7**	1.20	–	irreversible

[a] E_{pa}: Anodic sweep (peak potencials, Volts). – [b] E_{pc}: Cathodic sweep (peak potencials, Volts). – [c] Recorded in $NCCH_3$.

The decomposition behavior of the product molecules **5**−**7** is rather similar and the appearance of the curve depends on the total mass of the metal atoms (Figure 2). All product compounds first loose their carbonyl ligands. The total mass loss during the first decomposition step is roughly comparable to the CO content of the molecules, as also observed in the case of the $[NCMo(CO)_5]Na$ precursor molecule. The onset temperatures for the first decomposition step are ca. 100, 110 and 160°C respectively, in the case of **5**, **6** and **7**. In the first decomposition step no indication for the formation of $M(CO)_6$ as a thermal decomposition product has been detected. During the second decomposition step fragments of the pivalate ligand can be observed, especially $[C(CH_3)_3]^+$, $[H_2CCCH_2]^+$, $[H_2CCH]^+$ and $[CH_3]^+$. Carbon dioxide can also be found in significant amounts during the second decomposition step. Trace amounts of HCN^+ ($m/z = 27$) have also been detected during the second decomposition step of the complexes **5**−**7**. The onset temperatures for the second step are ca. 360, 390 and 270°C, respectively, for **5**, **6** and **7**. A small amount of pivalate fragments, however, can already be found during the first decomposition step. The intensity is nearly one order of magnitude smaller than during the second decomposition step. The remaining mass at the end of the measurement at 550°C is 44.6%, 49.3% and 61.9%, respectively. The mass of the metal atoms and the CN groups together is 43.5%, 47.4% and 53.7% in the cases of **5**−**7**. Taking into account the results of the simultaneous mass spectrometry this shows that the majority of the CO and the pivalate ligands is removed during the heating process. Replacement of the axial Cl ligands by $[(CO)_5M-CN]^-$ ligands clearly lowers the thermal stability of the resulting complex in comparison to its precursor.

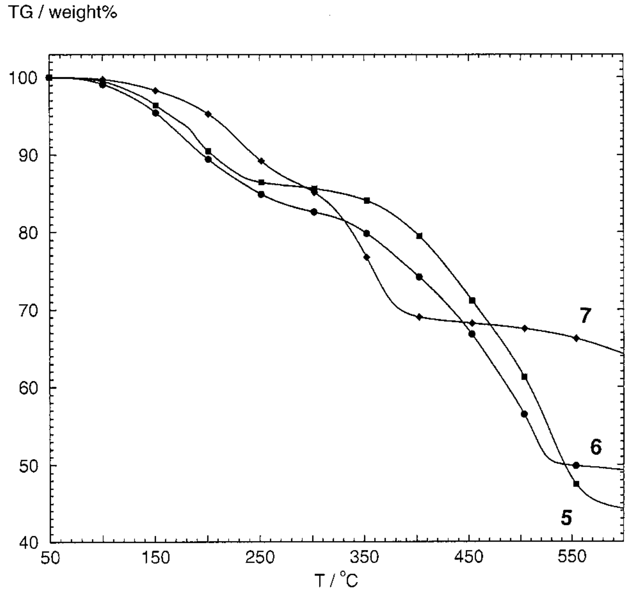

Figure 2. TG curves of $Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4[-NC-M(CO)_5]_2$ [M = Cr (**5**), Mo (**6**), W (**7**)]

Absorption Spectra

The UV/Vis absorption spectra of the compounds **5**−**7** are represented in Figure 3. The trace lines correspond to the absorption spectrum of the dichlorodirhenium tetrapivalate **1**, the point lines to the absorption spectra of the mononuclear complexes $[(CO)_5M-CN]Na$ [M = Cr (**2**), Mo (**3**), W (**4**)], and the full lines to the respective tetranuclear compounds. Comparison of the absorption spectra of these last species with the sum of the spectra of their components (two $[(CO)_5M-CN]^-$ units plus the dirhenium moiety) shows the appearence of new absorption bands that extend to the near-infrared region. These types of bands have been observed in similar compounds[6j] and can be attributed to MMCT transitions from the $[(CO)_5M-CN]^-$

units to the Re^{III} centers, on the basis of the NMR, IR and CV data.

Irradiation on these MMCT bands does not give any significant reaction followed in the visible spectral region.

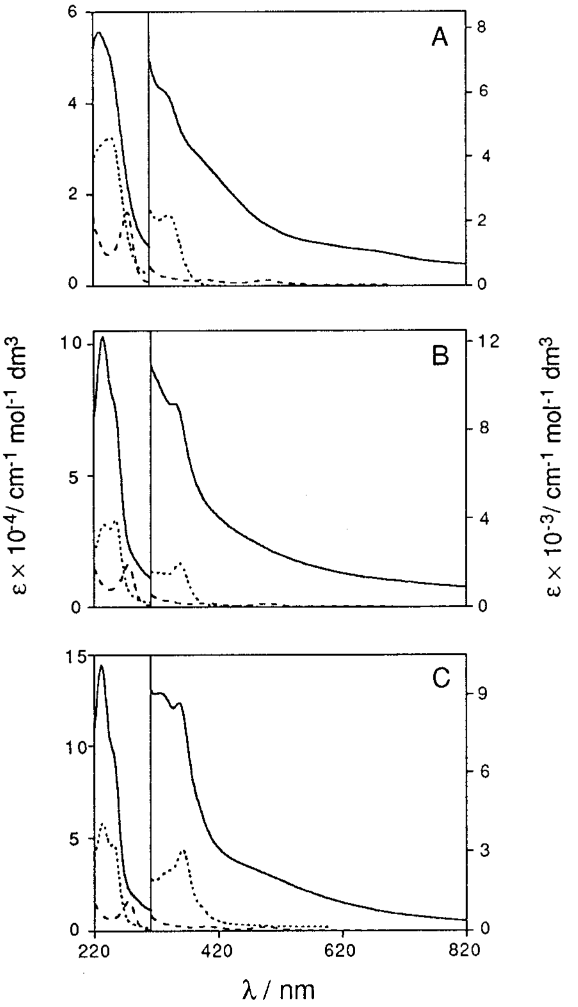

Figure 3. Absorption spectra of compounds **5** (**A**, full line), **6** (**B**, full line) and **7** (**C**, full line and their components **1** (**A**,**B**,**C**, point line), **2** (**A**, trace line), **3** (**B**, trace line) and **4** (**C**, trace line), in CH_3CN

Conclusions

Molecules of the type $[(CO)_5M-CN]^-$ not only form complexes with mononuclear metal centers, as described in the literature during the recent years, but also with dinuclear complexes containing metal−metal multiple bonds. Charge transfer between the ligands and the multiple bonded core unit takes place as can be judged from the optical absorption spectra. Significant charge donation from the $[(CO)_5M-CN]^-$ ligands to the ReRe core is also implied by ^{13}C- and ^{95}Mo-NMR as well as by cyclic voltammetry data. The Re−Re quadruple bond is only slightly weakened due to the donor influence of the organometallic ligand in the axial position. The synthesis of the described molecules is straightforward. An introduction of more NC functions in the ligands could therefore lead to long chained molecules with conjugated multiple bonds. It can also be assumed that it is easily possible to substitute other compounds of the type $[M_2(O_2CR)_4][X_2]$ or $[M_2(CH_3CN)_{10}][X_4]$ (M = Re, Rh, Mo, Tc, etc., X = BF_4, SF_6 etc.) with $[(NO)_xM(CO)_{6-x}]^-$ ligands. Work in this direction is currently under way in our laboratories and will be reported elsewhere.

Experimental Section

General: All preparations and manipulations were performed with standard Schlenk techniques under oxygen- and water-free argon. Solvents were dried by standard procedures: THF, Et_2O, *n*-pentane, and *n*-hexane with sodium benzophenone ketyl; acetonitrile and dichloromethane were distilled from P_2O_5 after refluxing for several hours. Acetone was distilled from K_2CO_3 and kept over 4-Å molecular sieves. − Microanalyses were performed at the ITQB (Oeiras). − ^1H-NMR spectra were obtained with a Bruker CXP 300 spectrometer, ^{13}C-NMR spectra were measured at 100.28 MHz with a JEOL JNM GX-400 and a Bruker Avance DPX-400, ^{95}Mo-NMR spectra were measured at 26.07 MHz with a Bruker Avance DPX-400. − Infrared spectra were recorded with a Unican Mattson Mod 7000 FTIR spectrophotometer using KBr pellets and/or solutions. − The TG/MS studies were performed using a Perkin Elmer TGA 7 thermobalance coupled with a Balzers QMG 420 mass spectrometer. The thermolysis experiments were carried out in a dynamic helium atmosphere (purity 5.0, 45 sccm) using a 50 to 600°C temperature program at a rate of 10°C/min. The temperature of the capillary interface was 280°C. − The electrochemical instrumentation consisted of a BAS CV 50W−1000 Voltammetric Analyzer connected to BAS/Windows data acquisition software. All the electrochemical experiments were run under argon at room temperature. Tetrabutylammonium hexafluorophosphate (Aldrich) was used as supporting electrolyte after being recrystallized from ethanol. Cyclic voltammetry experiments were performed in a glass cell MF-1082 from BAS in a C-2 cell enclosed in a Faraday cage. The reference electrode was SSC (MF-2063 from BAS). In all cases the calibration of the reference eletrode was performed with a solution of ferrocene (1mM) to obtain a potential in agreement with the literature value. The auxiliary electrode was a 7.5-cm platinum wire (MW-1032 from BAS) with a gold-plated connector. The working electrode was a disk of platinum (MF-2013 from BAS) with ca. 0.022 cm^2 sealed in Kel-F plastic. Solvents were dried as previously described.

Photochemical Studies: All solutions (ca. 10^{-3} M) were prepared and handled in the dark. Electronic absorption spectra were run using a Perkin Elmer lambda 6 UV/Vis spectrophotometer. The photochemical reactivity was initially tested at $\lambda \geqslant 600$ nm, $\lambda \geqslant 540$ nm. Even after longer irradiation times (> 24 h), no significant spectral changes were observed. Further irradiations were than carried out to check the photochemical reactivity at $\lambda = 436$ nm and $\lambda = 366$ nm. Irradiation experiments at $\lambda \geqslant 600$ nm and $\lambda \geqslant 540$ nm were carried out with a tungsten lamp and filters with cut-off at 600 and 540 nm, respectively. Irradiation experiments at 436 nm and 366 nm, were carried out in PTI instrumentation, using a medium-pressure Hg lamp (HBO 100 W) mounted in a lamphouse (Model A1010) connected to an LPS-220 Lamp Arc Supply. The light, whose intensity was of the order of 10^{-7} Einstein min^{-1},was isolated from the medium-pressure Hg lamp by means of interference filters P/N 56450 with $\lambda_{max} = 435.8$ nm, and P/N 56430 9 BAGT with $\lambda_{max} = 367$ nm, both from Allied Electro Optics

(Italy). − Raman spectra were measured at room temperature with a Renishaw imaging microscope 2000, equipped with a 25-mW Spectra Physics 127 HeNe excitation laser (632.8 nm); resolution of 1 cm^{-1}. − $[(CO)_5M-CN]Na$ (M = Mo, Cr, W)[10] and $Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4Cl_2$[11] complexes were prepared as described in the literature.

Spectroscopic data already given in the Tables 1−5 are not repeated in the Experimental Section.

Preparation of Complexes of General Formula $Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4[-CN-M(CO)_5]_2$ [M = Cr (5), Mo (6), W (7): A suspension of $Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4Cl_2$ (0.43 g, 0.50 mmol) in THF (15 mL), was treated with 1.00 mmol of $[(CO)_5M-CN]Na$ (M=Mo, Cr, W). The mixture turned dark red. After 90 min at room temperature, the resulting solution was concentrated to dryness, extracted with dichoromethane and concentrated. Upon addition of *n*-pentane, a dark red microcrystalline powder precipitated The mother liquor was filtered off and the remaining solid was dried in oil-pump vaccuum. Yield: 91% (**5**), 89% (**6**), 86% (**7**).

$Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4[-CN-Cr(CO)_5]_2$ (5): $C_{32}H_{36}Cr_2N_2O_{18}Re_2$ (1213.05): calcd. C 31.69, H 2.99, N 2.31; found C 31.78, H 3.13, N 2.02. − ^1H NMR (CD_2Cl_2, 300 MHz, +25°C): $\delta = 1.52$ (s, 9 H, 3 Me).

$Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4[-CN-Mo(CO)_5]_2$ (6): $C_{32}H_{36}Mo_2N_2O_{18}Re_2$ (1300.91): calcd. C 29.54, H 2.79, N 2.15; found C 29.77; H 3.10; N 2.06. − ^1H NMR (CD_2Cl_2, 300 MHz, room temp.): $\delta = 1.52$ (s, 9 H, 3 Me). − ^{95}Mo NMR (CD_2Cl_2, 400 MHz, +25°C): $\delta = -1690$.

$Re_2\{\mu\text{-}O_2CC(CH_3)_3\}_4[-CN-W(CO)_5]_2$ (7): $C_{32}H_{36}N_2O_{18}Re_2W_2$ (1476.76): calcd. C 26.03, H 2.46, N 1.90; found C 26.09; H 2.65; N 1.83. − ^1H NMR (CD_2Cl_2, 300 MHz, +25°C): $\delta = 1.52$ (s, 9 H, 3 Me).

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