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Journal of Organometallic Chemistry 560 (1998) 117–124

Journal of Organo metallic Chemistry

Synthesis and characterization of binuclear transition metal–rhenium(VII) complexes with bridging cyanide ligands

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Received 21 November 1997; received in revised form 27 January 1998

Abstract

Reacting transition metal complexes in low oxidation states, containing one or two cyanide ligands, with methyltrioxorhenium(VII) leads to bridged mixed metal compounds in good yields. The Re(VII) core is then surrounded by five or six ligands, respectively. The strength of these CN bridges and thus the stability of the newly generated bimetallic compound strongly depends on the donor strength of the ligands surrounding of the Cr/Mo/W or Fe moiety. The stability of the mixed metal molecules is reflected in the temperature dependent behavior of their ^{17}O-NMR spectra, in their IR (Re=O) stretching frequencies and force constants, as well as several other spectroscopic data. UV–vis absorption spectra show the appearance of charge transfer bands. In the case of the mixed Mo/Re complexes the ^{95}Mo-NMR spectroscopy is also a helpful tool to examine the donor capability of the Mo moiety. The described compounds also show photosensitivity. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cyanide bridges; Re(VII) oxides; Fe/Re binuclear complexes; Mo/Re binuclear complexes

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1. Introduction

Bridging cyanides involving linear M–C≡N–M′ arrangements are a prime object of studies of charge transfer, energy transfer and spin-exchange between the metal ions. Due to its electronic characteristics, the bridging cyanide ligand has been the subject of several recent investigations. Molecules containing metal atoms linked by one or more cyanide bridges are known [1].

Since it is also well established that methyltrioxorhenium(VII) (MTO) and related complexes readily form adducts with several organic and organometallic donor molecules [2], we were tempted to examine the behavior of this molecule in the presence of organometallic donors containing cyano ligands. MTO is an ideal acceptor molecule for investigation with different donor ligands because it has been shown that the chemical shift of its oxygen ligands in ^{17}O-NMR spectroscopy is strongly influenced by the donor capability of the coordinating ligands [3]. These chemical shift changes have proven to be significantly more sensitive than the changes in bond length detectable by single crystal X-ray determination [4]. It is also easily possible to follow the changes of the electron density around the Re(VII) core by UV–vis [5] and IR spectroscopy [6]. In this work we report the preparation and spectroscopic properties of complexes of general formula $Cp(L)_2Fe{-}CN{-}Re(CH_3)O_3$ (L = 0.5dppe, CO), $[(CO)_5M{-}CN{-}Re(CH_3)O_3]^-$ (M = Cr, Mo, W) and $[CpMo(CO)_2({-}CN{-})_2Re(L)O_3]K$ [L = Cl, Br, CH_3]. The ^{1}H-, ^{17}O-, ^{95}Mo-NMR, IR and UV–vis spectra and

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PII S0022-328X(98)00495-1

Table 1
Selected IR (cm^{-1}) and ^{1}H-NMR data (ppm) of mononuclear and binuclear complexes

Compound		$\delta(^1H)$Cp	$\delta(^1H)$Me	$\nu(C\equiv O)$	$\nu(C\equiv N)$
Cp(dppe)Fe–CN		4.20	—	—	2062
Cp(dppe)Fe–CN–Re(CH_3)O_3	**1**	4.24	2.74	—	2074
Cp(CO)$_2$Fe–CN		5.07	—	2056, 2006	2118
Cp(CO)$_2$Fe–CN–Re(CH_3)O_3	**2**	5.14	2.55	2058, 2006	2158
[Cp(CO)$_2$Mo(–CN)$_2$]K		5.32	—	1966, 1883	2102[b]
[Cp(CO)$_2$Mo(–CN–)$_2$Re(Cl)O_3]K	**3**	—	—	1981, 1915	2122
[Cp(CO)$_2$Mo(–CN–)$_2$Re(Br)O_3]K	**4**	—	—	1979, 1913	2122
[Cp(CO)$_2$Mo(–CN–)$_2$Re(CH_3)O_3]K	**5**	—	2.05	1971, 1892	2109
CH_3ReO_3[a]		—	2.81	—	—

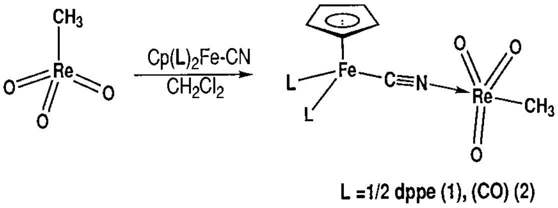
All ^{1}H-NMR spectra were recorded in CH_3NO_2 at r.t.

[a] Data taken from refs. [3,6]. [b] $\nu(C\equiv N)_{asym}$ stretch hidden under $\nu(C\equiv O)$ peaks.

photochemical examinations of selected molecules are presented and discussed.

2. Results and discussion

The addition of the cyanide ligands Cp(dppe)Fe–CN and Cp(CO)$_2$Fe–CN to MTO in CH_2Cl_2 immediately leads to orange solutions from which the heterobinuclear complexes Cp(dppe)Fe–CN–Re(CH_3)O_3 (**1**) and Cp(CO)$_2$Fe–CN–Re(CH_3)O_3 (**2**) are isolated as brown–yellow solids in good yields (Eq. 1). The compounds are stable at room temperature (r.t.) but decompose slowly in the presence of air and moisture. As it is well known for the decomposition of several organorhenium(VII) oxide derivatives perrhenates are formed by the water induced decomposition process [4].



(1)

The ^{1}H-NMR spectra of the compounds **1** and **2** were recorded in CD_3NO_2 at r.t. (see Table 1). The Cp protons of **1** and **2** appear as singlets at δ 4.24 and 5.14 ppm, respectively. In comparison with the uncomplexed Fe compounds, coordination to MTO leads only to a slight field shift of ca. 0.1 ppm for the chemical shift of the Cp protons. The chemical shifts of the methyl protons appear at higher field then those of uncoordinated MTO in the same solvent. The shift differences of the CH_3-protons in **1** and **2** are due to the electron donor capability of the Fe ligand complexes. It has to be noted, however, that these shift changes are small in comparison to several organic Lewis bases, e.g. pyridine {$\delta(^1H)$ of the MTO–CH_3 group is 1.68 ppm [3]}.

Selected peaks observed in the IR spectra of these compounds, recorded in KBr, are given in Table 1. The Re=O stretching vibrations clearly indicate the coordination to MTO by an electron donor. In contrast to the ^{1}H-NMR data, the IR data indicate a stronger coordination than in most known monodentate organic Lewis base adducts of MTO. Typical values of Re=O force constants in these cases lie in the range 8.3–8.1 ([4]a, [6]). In the cases of compounds **1** and **2**, the force constants are around 7.5 mdyn/Å (see Table 2). As expected, the stronger electron donor Cp(dppe)Fe–CN leads to a stronger Fe–CN → Re interaction, resulting in a lower Re=O force constant in **1** when compared with that of **2**.

As a consequence of the formation of a Fe–C≡N → Re bridge, the $\nu(C\equiv N)$ bands of the complexes Cp(dppe)Fe–CN–Re(CH_3)O_3 (**1**) and Cp(CO)$_2$Fe–CN–Re(CH_3)O_3 (**2**) occur at higher wavenumbers than the $\nu(C\equiv N)$ bands of the non-coordinated iron complexes, Cp(dppe)Fe–CN and Cp(CO)$_2$Fe–CN (Table 1). However, this shift is much higher for **2** (40 cm^{-1}) than for **1** (12 cm^{-1}).

The factors that affect bridging $\nu(C\equiv N)$ frequency shifts have been discussed ([1]l). Besides being expected for any bridging CN ligand the shift observed in **2** is typical of M–CN–M′ bridges in which the M′ fragment is a Lewis acid. No change in backdonation from the CpFe(CO)$_2$ moiety to the CN is observed as the $\nu(C\equiv O)$ vibrations of this fragment remain virtually unchanged upon complexation. On the contrary, the Cp(dppe)Fe fragment of the Cp(dppe)Fe–CN ligand, considered as

Table 2
Force constants F(Re=O) [mdyn/Å] and IR vibrations ν(Re=O) of complexes **1**–**5**

Compound		F(Re=O)	ν(Re=O)
Cp(dppe)Fe–CN–Re(CH_3)O_3	**1**	7.50	955 s, 918 vs
Cp(CO)$_2$Fe–CN–Re(CH_3)O_3	**2**	7.56	962 s, 920 vs
[Cp(CO)$_2$Mo(–CN–)$_2$Re(Cl)O_3]K	**3**	7.26	927 w, 911 vs
[Cp(CO)$_2$Mo(–CN–)$_2$Re(Br)O_3]K	**4**	7.18	926 w, 905 vs
[Cp(CO)$_2$Mo(–CN–)$_2$Re(CH_3)O_3]K	**5**	8.12	988 m, 950 vs

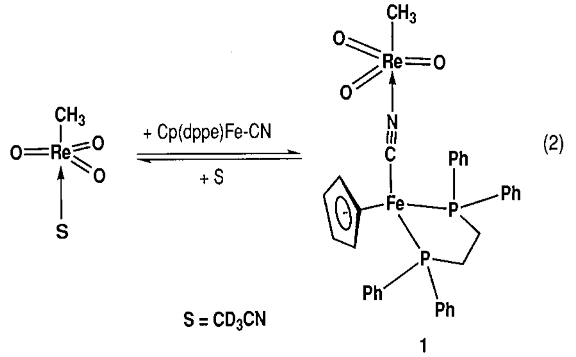
Table 3
^{17}O-NMR data of selected M–CN–Re complexes

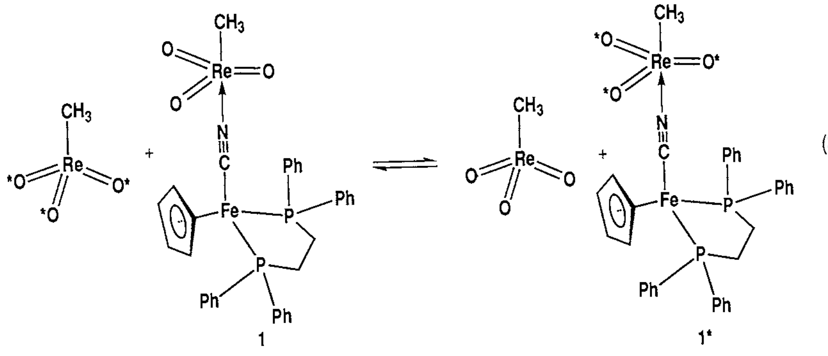
T (°C)	Chemical shift (ppm)	Half width (Hz)
Cp(dppe)Fe–CN–Re(CH_3)O_3 in CD_3CN[a]		
+75	807	96
+25	801	148
±0	794	201
−40	789	480
Cp(dppe)Fe–CN–Re(CH_3)O_3+excess MTO (1:3) in CD_3CN[a]		
+75	821	52
+20	821	70
−40	824	192
Cp(CO)$_2$Fe–CN–Re(CH_3)O_3 in CD_3CN[a]		
+75	825	35
+20	827	44
−40	832	87
[Cp(CO)$_2$Mo(–CN–)$_2$Re(CH_3)O_3]K in CD_3NO_2[a]		
+80	819	50
+25	816	65
−25	814	105
[(CO)$_5$Cr–CN–Re(CH_3)O_3]Li in CD_3OD[a]		
−25	797	310
+20	724[b]	370
[(CO)$_5$Mo–CN–Re(CH_3)O_3]Na in CD_3OD[a]		
−25	830	240
+20	809[b]	520
[(CO)$_5$W–CN–Re(CH_3)O_3]Li in CD_3OD[a]		
−25	735	230
+20	697[b]	380

[a] Chemical shifts of MTO: $\delta(^{17}O) = 824$ ppm (CD_3CN), 819 ppm (CD_3NO_2), 861 ppm (CD_3OD) [3]. [b] Partial decomposition starts already below r.t.

extremely electron rich ([1]c), must provide significant backdonation to the bridging cyanide, almost overriding the kinematic shift to higher frequencies ([1]l).

^{17}O-NMR spectroscopy performed in CH_3CN also shows that complex **1** has a stronger Fe–C≡N→Re interaction than complex **2** (Table 3). This is especially evident at low temperature. Usually, weak donor ligands coordinated to MTO in the solid state are easily replaced by strong donor solvents, e.g. pyridine, THF or CH_3CN (Eq. 2). Cooling down the solution slows this exchange and shifts the equilibrium to the right side if the coordinating complex is a stronger donor than the solvent [3]. In the case of compound **1**, the ^{17}O-NMR shift changes from 807 ppm at 75°C to 789 ppm at −40°C. In the case of complex **2**, however, the chemical shift does not change significantly in the same temperature range. If a 3-fold excess of ^{17}O-labelled MTO is added to a solution of unlabelled Cp(dppe)Fe–CN–Re(CH_3)O_3, neither the signal of uncoordinated MTO [$\delta(^{17}O)$ 825 ppm] nor the signal of **1** [$\delta(^{17}O)$ 801 ppm] can be observed both being reflected by an averaged signal at ca. 820 ppm. Also, cooling down or warming up the solution does not change the chemical shift significantly. When stoichiometric amounts of labelled MTO and labelled **1** are mixed, the ^{17}O-NMR signal appears at 816 ppm. In the proton NMR spectrum a broad peak between the signal MTO and the signal of **1** can be observed. The known signals of both components of the mixture do not show up. The reason for these observations must be a second exchange equilibrium, as shown in Eq. 3. Similar equilibria are known for organorhenium(VII) oxides coordinated by organic Lewis bases ([3]b).





The adducts were also characterised by means of their electronic absorption spectra, depicted in Fig. 1. In the case of compound **2**, the spectrum of the adduct is coincident with the sum of the spectra of each component, MTO and Cp(CO)$_2$Fe–CN. In the case of compound **1**, however, the formation of a low intensity new absorption band, centered at ca. 500 nm ($\varepsilon = 30$ M^{-1} cm^{-1}), can be observed. This band can, in principle, be attributed to a charge transfer from the donor moiety, Cp(dppe)Fe–CN, to the acceptor, MTO, as described for $[Fe(CN)_6]^{2-}$ and MTO ([5]c). The observation of a charge transfer (CT) band in compound **1** and its absence (for $\lambda > 400$ nm) in compound **2** are in agreement with the IR and ^{17}O-NMR data reported above, reflecting the stronger electron donor character of Cp(dppe)Fe–CN in comparison to $Cp(CO)_2Fe$–CN.

In order to improve the interaction of CN bridges with $Re(X)O_3$ molecules, we considered $[Cp(CO)_2Mo(-CN)_2]^-$ as a good ligand because it may act as a bidentate ligand and bears a negative charge. As a matter of fact, both its $\nu(C{\equiv}O)$ and $\nu(C{\equiv}N)$ stretching frequencies appear at lower frequencies that those of $Cp(CO)_2Fe$–CN (Table 1).

Therefore the complexes $[Cp(CO)_2Mo(-CN-)_2Re(X)O_3]K$, with X = Cl (**3**), Br, (**4**) CH_3 (**5**), (Eq. 4) were prepared. In the case of compounds **3** and **4** the products precipitate immediately after their formation, thus shifting the equilibrium completely to the product side. However, the insolubility of **3** and **4** in all common organic solvents prevented NMR and UV–vis studies. The IR spectra of both compounds, recorded in KBr matrix, indicate a distorted octahedral coordination of the rhenium center in the solid state, as it was expected for bidentate coordination of the $[Cp(CO)_2Mo(-CN)_2]^-$ ligand. The force constants of the complexes were calculated from the Re=O vibration bands to be 7.26 and 7.18 mdyn/Å and are, therefore, in the same order of magnitude as 2,2′-bipyridine adducts of organorhenium(VII) oxides and rhenium(VII) halide oxides (they usually range 7.45–7.30 mdyn/Å ([4]a, [6,7])). In the case of the soluble compound **5**, the Mo–CN–Re interaction is significantly weaker. The ^{95}Mo-NMR signal is only shifted 10 ppm, from −200 ppm in the free Mo precursor compound to −190 ppm in complex **5**. The signal is extremely broad (ca. 4000 Hz). The ^{17}O-NMR data also show only a minor shift difference from uncoordinated MTO [$\delta(^{17}O) = 819$ ppm] to compound **5** [$\delta(^{17}O) = 814$ ppm] in d^3-nitromethane at −25°C. Warming the solution leads to an even smaller shift difference [$\delta(^{17}O) = 816$ ppm at r.t.]. These data again emphasize the weak coordination of the Re(VII) center by the CN functions in this case. In the ^1H-NMR the $Re-CH_3$ signal is shifted from $\delta(^1H) = 2.81$ (free MTO) to 2.05 ppm spectrum of complex **5**. For an octahedrally-coordinated $R-ReO_3 \cdot L$ complex the latter chemical shift is still an indication for a weak coordination. Typical chemical shifts of the $Re-CH_3$ group with strongly coordinating organic ligands are ca. 1.5 ppm ([4]a, [6,7]). The differential UV–vis spectrum of a mixture of CH_3ReO_3 and $[Cp(CO)_2Mo(-CN)_2]^-$ in MeOH, both 0.01 M, and the sum of the spectra of the separated components (0.01 M) shows the tail of a band at $\lambda < 500$ nm, also indicating that some interaction occurs.

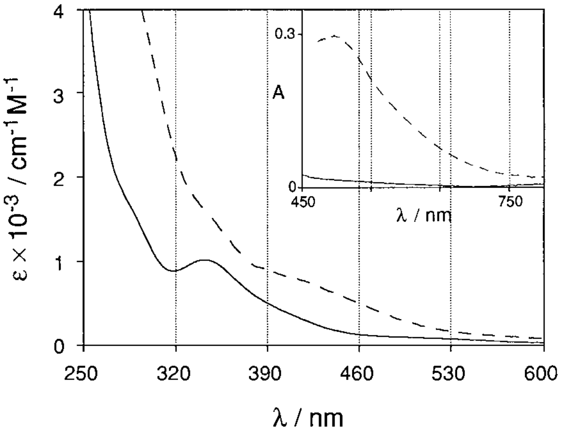
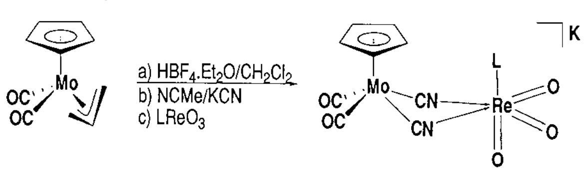


Fig. 1. UV–vis absorption spectra of the heterobinuclear complexes Cp(dppe)Fe–CN–$Re(CH_3)O_3$ (- -) (**1**) and $Cp(CO)_2Fe$–CN–$Re(CH_3)O_3$ (—) (**2**). In the inset: absorption differential absorption spectrum between a methanolic solution 0.01 M in both Cp(dppe)Fe–CN and MTO and the sum of the spectra of the separated components (- -); the same applies for $Cp(CO)_2Fe$–CN and MTO (—).



(4)

L = Cl (**3**), Br (**4**), CH_3 (**5**)

The IR spectrum of compound **5** also supports our statement that the Mo–CN–Re interaction is weak. The Re=O force constant is 8.12 mdyn/Å, thus only slightly weaker than in uncoordinated MTO (F(ReO) = 8.31 mdyn/Å). The ν(CO) IR vibrations also clearly show the difference between the coordinated Mo complexes **3** ($\nu(CO) = 1981$ and 1915 cm^{-1}) and **4** ($\nu(CO) = 1979$ and 1914 cm^{-1}) and the uncoordinated precursor compound ($\nu(CO) = 1966$ and 1884 cm^{-1}). Coordination to the electron withdrawing Re(VII) centre causes a weakening of the backdonation to the CO ligands as judged from the increase of the ν(CO) frequencies in **3** and **4** relative to ν(CO) in the electron richer starting material. The back donating effect of the Mo orbitals to the π^*-orbitals is somewhat stronger in the case of $[Cp(CO)_2Mo(-CN)_2]^-$, therefore reducing the total bond order in the carbonyl slightly and weakening the C≡O bond. In the case of complex **5** this ν(CO) is smaller $\nu(CO) = 1971$ and 1892 cm^{-1}. This again supports the already mentioned weaker coordination of the Re(VII) center by the cyano functions in complex **5** in comparison to **3** and **4**. The electron withdrawing effect of the $Re(VII)O_3$ moiety is also mirrored in the $\nu(C{\equiv}N)$ vibration of the molecules **3**–**5**. The corresponding signal is shifted from 2103 cm^{-1} in the starting material to 2122 cm^{-1} in the products **3** and **4** and 2109 cm^{-1} in compound **5**.

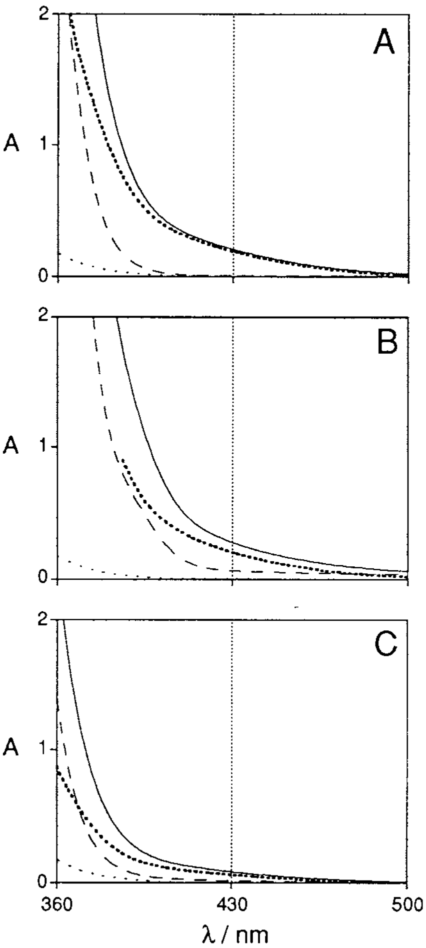
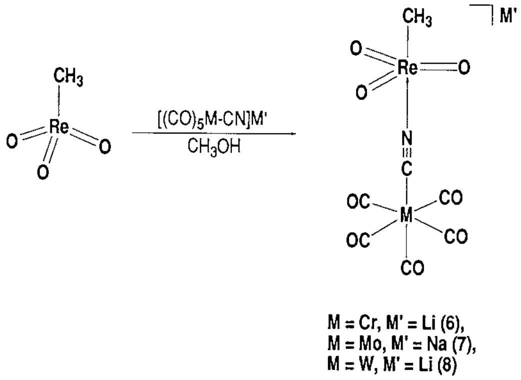


Fig. 2. UV–vis absorption spectra of 0.01 M methanolic solutions of (1) MTO (. . .), (2) $[(CO)_5M{-}CN]Na$ (- -), (3) MTO + $[(CO)_5M{-}CN]Na$ (—), and differential spectra between (3) and (2) + (1) (. . .). M = Mo (**A**), W (**B**), Cr (**C**).

In attempting to get some more soluble binuclear $M{-}CN{-}Re(L)O_3$ complexes, the anions $[(CO)_5M{-}CN]^-$ were reacted with MTO, according to Eq. 5. Both starting materials, MTO and $[(CO)_5Mo{-}CN]Na$, are colorless compounds. Mixing them in THF or diethyl ether immediately leads to a color change to yellow, a typical color for Lewis base adducts of MTO when colorless starting materials (e.g. bipy, quinuclidine) are used [3]. The appearance of the yellow color upon mixing the two compounds was monitored by UV–vis absorption spectroscopy (Fig. 2). Inspection of this figure clearly shows that the absorption spectrum of the mixture is not coincident with the sum of the separated components. This result is similar to those observed above and suggests that in this case formation of a charge transfer type adduct between $[(CO)_5M{-}CN]^-$ (M = Cr, Mo, W) and MTO also occurs. The products with the formulae $[(CO)_5M{-}CN{-}Re(CH_3)O_3]M'$ {M = Cr, M′ = Li (**6**), M = Mo, M′ = Na (**7**), M = W, M′ = Li (**8**)} are orange–yellow, moisture and temperature sensitive, turning brown within ca. 5 min if left at r.t. In the presence of water they turn white under formation of perrhenates. The proton NMR spectra of the complexes **6**–**8** show a significantly stronger M–CN → Re interaction then in compounds **2** and **5**. The chemical shifts of the rhenium bound methyl group are around 1.6 ppm in d^4-methanol, compared to 2.0 ppm of free MTO in methanol (methanol is itself a coordinating solvent, forming an MTO–methanol adduct in solution [3]). The ^{17}O-NMR results (see Table 3) and the ^{95}Mo data (see Table 4) of complex **6** support the statement concerning the stronger coordination of complexes **6**–**8**. IR spectra could not be obtained due to the thermal instability of the complexes.



(5)

Attempts to carry out photochemical studies in order to obtain the reduced electron acceptor species {ReO_4^- or ReO_3 ([5]a,b)} and the oxidized donor, were not successful by the following reasons: (i) in compounds **1**, **2** and **5**, selective excitation on the new CT band is not possible; in addition, they are not thermally stable and (ii) in compounds **6**, **7**, and **8**, selective excitation is possible but as in the previous examples the thermal degradation strongly competes with the photochemical reaction.

Table 4
^{95}Mo-NMR data for $[(CO)_5Mo{-}CN{-}Re(CH_3)O_3]Na$ (**7**) and $[(CO)_5Mo{-}CN]Na$ in CD_3OD[a]

T (°C)	Chemical shift(ppm)	Half width (Hz)
$[(CO)_5Mo{-}CN]Na$		
−25	−1892	190
+25	−1882	130
+60	−1875	190
$[(CO)_5Mo{-}CN{-}Re(CH_3)O_3]Na$		
−25	−1874	250
+25	−1865	190
+60	−1858	320

[a] Partial decomposition of complex **7** occurs already below r.t.

3. Conclusions

MTO and some inorganic Re(X)O_3 derivatives easily form charge transfer complexes with electron rich organometallic complexes via CN bridges. Depending on the number of the donor CN functions pentacoordinated or octahedral Re(VII) complexes are formed, as can be concluded from the spectroscopic results. When the cyano ligands are weak donors, the complexes show rapid temperature dependent ligand/solvent exchange. In the case of more strongly donating organometallic donor complexes the resulting molecules are more stable against donor ligand exchange but not necessarily against temperature. Given the easy preparation of all complexes described here our findings open a broad field for the synthesis of novel mixed metal complexes, which might present interesting photochemical properties.

4. Experimental section

All preparations and manipulations were performed with standard Schlenk techniques under an oxygen- and water-free argon atmosphere. Solvents were dried by standard procedures THF, Et_2O, pentane, and hexane over Na/benzophenone ketyl; acetonitrile and dichloromethane were distilled after refluxing for several hours over P_2O_5. Acetone was distilled over K_2CO_3 and kept over 4 Å molecular sieves. ^{1}H-NMR spectra were obtained with a Bruker CXP 300 and a Bruker Avance DPX-400 spectrometer. IR spectra were recorded on a Unican Mattson Mod 7000 FT-IR spectrophotometer and a Perkin-Elmer FT-IR spectrometer using KBr pellets as IR matrix. ^{17}O-NMR spectra were measured at 54.14 MHz on a JEOL JNM GX-400 and ^{95}Mo-NMR at 26.07 MHz on a Bruker Avance DPX-400. Elemental analyses were performed in the Mikroanalytisches Labor of the TU München in Garching and by J.P. Lopes at the ITQB, Oeiras. ^{17}O-marked Re_2O_7 and CH_3ReO_3 were prepared according to the literature [3,8]. CpMo(η^3-C_3H_5)$(CO)_2$ [9], Cp(dppe)Fe–CN [10], $Cp(CO)_2Fe$–CN [11], $[(CO)_5M–CN]^-$ (M = Cr, Mo, W) [12] were prepared as described previously.

4.1. Photochemical studies

All solutions were prepared and handled in the dark. Electronic absorption spectra were run on a Perkin Elmer lambda 6 UV–vis spectrophotometer. Irradiation experiments were carried out in PTI instrumentation, using a medium pressure Hg lamp (HBO 100 W) mounted in a lamphouse (Model A1010) connected to a LPS-220 Lamp Arc Supply. Light of 436 nm was isolated from the medium pressure Hg lamp by means of an interference filter (P/N 56450 Allied Electro Optics (Italy); $\lambda_{max} = 435.8$ nm).

4.2. Preparation of Cp(dppe)Fe–CN–Re(CH_3)O_3 (**1**)

A solution of CH_3ReO_3 (0.20 g, 0.80 mmol) in CH_2Cl_2 (5 ml) was treated with a solution of Cp(dppe)Fe–CN (0.43 g, 0.80 mmol) in the same solvent. After 15 min the dark yellow solution was concentrated to ca. 5 ml and addition of ether precipitated the product. The mother liquor was filtered off and the remaining precipitate was washed with diethyl ether/*n*-pentane and dried in vacuum. Yield 0.57 g (90%). Anal. Calc. for $C_{33}H_{32}NP_2O_3FeRe$ (794.63): C 49.88, H 4.06, N 1.76. Found: C 50.10, H 4.40, N 1.91%. Selected IR (KBr, ν cm^{-1}): 3055 m, 2955 m, 2074 vs (N≡C), 1463 m, 1435 s, 1096 s, 1011 m, 955 s, [sym (Re=O)], 918 vs [asym (Re=O)], 744 s, 696 s, 532 s. ^{1}H-NMR (CD_3NO_2, 300 MHz, r.t., δ ppm): 7.53–7.07 (m, 20H, dppe), 4.24 (s, 5H, Cp), 2.74 (s, 3H, Me), 2.56–2.33 (m, 4H, $-CH_2$). ^{17}O-NMR (−40°C, CD_3CN, δ ppm): 789. ^{31}P-NMR (CH_3CN, r.t., δ ppm): 102 (s).

4.3. Preparation of $Cp(CO)_2Fe$–CN–Re(CH_3)O_3 (**2**)

A solution of CH_3ReO_3 (0.20 g, 0.80 mmol) in CH_2Cl_2 (5 ml) was treated with a solution of $Cp(CO)_2Fe$–CN (0.16 g, 0.80 mmol) in the same solvent. After 20 min the orange–yellow solution was concentrated to ca. 5 ml and addition of ether precipitated the product. The mother liquor was filtered off and the remaining precipitate was washed with diethyl ether/*n*-pentane and dried in vacuum. Yield 0.35 g (98%). Anal. Calc. for $C_9H_8NO_5FeRe$ (452.22): C 23.90, H 1.78, N 3.10. Found: C 23.84, H 1.55, N 3.25%. Selected IR (KBr, ν cm^{-1}): 3117 m, 3015 m, 2158 vs (N≡C), 2058 vs (C≡O), 2006 vs (C≡O), 1427 m, 1009 m, 962 s, [sym (Re=O)], 920 vs [asym (Re=O)], 870 m, 837 m, 606 s, 563 s. ^{1}H-NMR (CD_3NO_2, 300 MHz, r.t., δ ppm): 5.14 (s, 5H, Cp), 2.55 (s, 3H, Me). ^{17}O-NMR (−25°C, CD_3CN, δ ppm): 832.

4.4. Preparation of $[Cp(CO)_2Mo(-CN)_2]K$

A solution of CpMo(η^3-C_3H_5)$(CO)_2$ (0.20 g, 0.77 mmol) in CH_2Cl_2 (20 ml) was treated with HBF_4Et_2O (one equivalent). After 10 min excess NCMe was added (2 ml) and the reaction left for 30 min at r.t. The mixture was taken to dryness and the solid, $[CpMo(NCMe)_2(CO)_2]BF_4$, dissolved in methanol:ethanol (5:10). Excess of KCN (0.13g, 2.00 mmol) was added and the mixture vigorously stirred for 6h. The resulting orange solution was filtered, evaporated to dryness, extracted with acetone and concentrated. Upon addition of *n*-pentane an oily residue separated which was solidified to a yellow microcrystalline power after scratching and repeated washings with pentane. Yield: 0.19 g (80%). Anal. Calc. for $C_9H_5N_2O_2KMo$ (308.19): C 35.08, H 1.64, N 9.09. Found: C 35.26, H 2.17, N 9.20%. Selected IR (KBr, ν cm^{-1}): 3111 m, 2102 s, 1966 vs, 1884 vs, 1695 m, 1423 m, 1092 m, 1014 m, 813 s, 536 s. ^{1}H-NMR (CD_3NO_2, 300 MHz, r.t., δ ppm): 5.32 (s, 5H, Cp). ^{95}Mo-NMR (-25°C, CD_3NO_2, δ ppm): -200.

4.5. Preparation of complexes of general formula [CpMo(CO)$_2$(–CN–)$_2$Re(X)O$_3$]K [X = Cl (**3**), Br (**4**)]

To solutions of Re_2O_7 (0.5 g, 1.03 mmol) in THF (10 ml), were added 1.03 mmol of Bu_4NX. The solution turned pale yellow. After 5 min, 1.03 mmol of [Cp(CO)$_2$Mo(–CN)$_2$]K were added and after a few seconds a yellow–brown precipitate formed. The precipitate was washed three times with 10 ml of diethyl ether and with 10 ml *n*-pentane. The remaining residue was dried in oil pump vaccum. Yield: 0.51 g (85%) (**3**) and 0.50 g (79%) (**4**).

[Cp(CO)$_2$Mo(–CN–)$_2$Re(Cl)O$_3$]K (**3**). Anal. Calc. for $C_9H_5N_2O_5KMoReCl$ (577.85): C 18.71, H 0.87, N 4.85. Found: C 18.95, H 1.01, N 4.79%. Selected IR (KBr, ν cm^{-1}): 2122 m, 1981 s, 1915 s, 927 w, 911 vs, 800 m.

[Cp(CO)$_2$Mo(–CN–)$_2$Re(Br)O$_3$]K (**4**). Anal. Calc. for $C_9H_5N_2O_5KMoReBr$ (622.30): C 17.37, H 0.81, N 4.50. Found: C 17.52, H 0.92, N 4.37%. Selected IR (KBr, ν cm^{-1}): 2122 m, 1979 s, 1914 s, 926 w, 905 vs, 798 m.

4.6. Preparation of [Cp(CO)$_2$Mo(–CN–)$_2$Re(CH$_3$)O$_3$]K (**5**)

To a solution of CH_3ReO_3 (250 mg, 1.00 mmol) in diethyl ether (4 ml), were added 1.00 mmol of [Cp(CO)$_2$Mo(–CN)$_2$]K. The solution turned brown immediately. After 30 min, the solution was cooled to -30°C and the solvent removed in oil pump vacuum. Removal of the solvent at r.t. leads to a color change to black within minutes. The residue was washed with 5 ml cold *n*-pentane, then dried again. Yield: 0.5 g (89%). Anal. Calc. for $C_{10}H_8N_2O_5KMoRe$ (557.34): C 21.55, H 1.45, N 5.03. Found: C 21.67, H 1.54, N 4.97%. Selected IR (KBr, ν cm^{-1}): 2984 m, 2898 m, 2109 m, 1971 s, 1892 s, 1359 m, 1262 m, 998 m, 950 vs, 802 m. ^{1}H-NMR (CD_3NO_2, 400 MHz, r.t., δ ppm): 5.58 (s, 5H, Cp), 2.05 (s, 3H, CH_3). ^{17}O-NMR (-25°C, CD_3NO_2, δ ppm): 814. ^{95}Mo-NMR (-25°C, CD_3NO_2, δ ppm): -190.

4.7. Preparation of complexes of general formula [(CO)$_5$M–CN–Re(CH$_3$)O$_3$]M′ [M = Cr (**6**), M′ = Li, Mo (**7**), M′ = Na, and W (**8**) M′ = Li]

To a solution of CH_3ReO_3 (250 mg, 1.00 mmol) in methanol (4 ml), were added 1.00 mmol of [(CO)$_5$M–CN]Li or [(CO)$_5$M–CN]Na, respectively at -20°C. The formerly colorless solutions turned orange–yellow. After 15 min the solvent was removed at -40°C in oil pump vacuum and the orange residue was washed with 5 ml cold *n*-pentane and dried in oil pump vacuum at -50°C. Yields: 0.3 g (65%) (**6**), 0.3 g (57%) (**7**), 0.43 g (71%) (**8**).

[(CO)$_5$Cr–CN–Re(CH$_3$)O$_3$]Li: Anal. Calc. for $C_7H_3NO_8LiMoRe$ (474.25): C 17.73, H 0.64, N 2.95. Found: C 18.16, H 0.68, N 2.89%. ^{1}H-NMR (CD_3OD, 400 MHz, -25°C, δ ppm): 1.66 (s, 3H, Me). ^{17}O-NMR (-25°C, CD_3OD, δ ppm): 797.

[(CO)$_5$Mo–CN–Re(CH$_3$)O$_3$]Na: Anal. Calc. for $C_7H_3NO_8NaMoRe$ (534.24): C 15.74, H 0.57, N 2.62. Found: C 15.99, H 0.78, N 2.91%. ^{1}H-NMR (CD_3OD, 400 MHz, -25°C, δ ppm): 1.67 (s, 3H, Me). ^{17}O-NMR (-25°C, CD_3OD, δ ppm): 830. ^{95}Mo-NMR (-25°C, CD_3OD_2, δ ppm): -1874.

[(CO)$_5$W–CN–Re(CH$_3$)O$_3$]Li: Anal. Calc. for $C_7H_3NO_8LiWRe$ (606.10): C 13.87, H 0.50, N 2.31. Found: C 13.61, H 0.62, N 2.54%. ^{1}H-NMR (CD_3OD, 400 MHz, -25°C, δ ppm): 1.56 (s, 3H, Me). ^{17}O-NMR (-25°C, CD_3OD, δ ppm): 735.

Acknowledgements

This work was supported by PRAXIS XXI, Projects (2/2.1/QUI/316/94 and 2/2.1/QUI/419/94). The authors want to thank the DAAD and CRUP (INIDA and Acções Integradas Programme) and Prof. W.A. Herrmann for generous support. I.S. Gonçalves (BPD) and A.D. Lopes (BD) thank PRAXIS XXI for grants, and F.E. Kühn acknowledges the Alexander von Humboldt foundation for financial support.

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