Interaction of decacarbonyldimanganese and decacarbonyldirhenium with 1-aryl-3-cyanoprop-2-en-1-ones

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The reactions of $M_2(CO)_{10}$ (M = Mn, Re) with *trans*-1-aryl-3-cyanoprop-2-en-1-ones in the presence of Me_3NO proceed with replacement of the CO ligand and lead to complexes *eq*-(1-aryl-3-cyanoprop-2-en-1-on)nonacarbonyldimanganese and *eq*-(1-aryl-3-cyanoprop-2-en-1-on)nonacarbonyldirhenium complexes where the metals are bonded with the ligand through the nitrogen atom of the cyanogroup. The treatment of (1-phenyl-3-cyanoprop-2-en-1-on)nonacarbonyldirhenium with a second equivalent of the ligand resulted in the disubstituted complex, *eq,eq*-bis(1-phenyl-3-cyanoprop-2-en-1-on)octacarbonyldirhenium in a good yield. The structures of the obtained complexes are discussed on the basis of ^{13}C, ^1H NMR, and IR-spectroscopy.

Key words: decacarbonyldimanganese and decacarbonyldirhenium, 1-aryl-3-cyanoprop-2-en-1-ones, *eq*-(1-aryl-3-cyanoprop-2-en-1-on)nonacarbonyldimanganese and *eq*-(1-aryl-3-cyanoprop-2-en-1-on)nonacarbonyldirhenium, *eq,eq*-bis(1-phenyl-3-cyanoprop-2-en-1-on)octacarbonyldirhenium, CO-substitution.

In a continuation of our investigations of the reactions of metal carbonyls with functionally substituted olefins,[1,2] we have studied the reaction of manganese and rhenium carbonyls $M_2(CO)_{10}$ with unsaturated ketones including those with the coordinating β-substituent, *viz.*, the cyanogroup.

RCOCH=CHR'

1a: R = Me; R' = Ph, **1b**: R = *n*-$CH_3C_6H_4$; R' = Ph,
1c: R = Ph; R' = CN, **1d**: R = o-ClC_6H_4; R' = CN.

Several examples of the photochemical reactions of $Re_2(CO)_{10}$ with olefins are known, which afford dirhenium complexes containing σ,π-vinyl bridges.[3,4] Reactions of this type have not been investigated for functionally substituted olefins.

The reactions of compounds **1a,b** with $Re_2(CO)_{10}$ were carried out using the main methods for replacement of the CO ligands in metal carbonyls, *i.e.*, thermal and photochemical methods as well as the action of Me_3NO. However, the reactions are accompanied by a dramatic decomposition, and it is impossible to isolate any carbonyl compound except for the starting $Re_2(CO)_{10}$.

Stable complexes were obtained only by the reactions of $M_2(CO)_{10}$ (M = Mn, Re) with the cyanosubstituted ketones **1c,d** in the presence of Me_3NO (Eq. (1)).

It is interesting that, regardless of the component ratio, the main reaction products are monosubstituted compounds **2a—d**, where, according to their spectral data (see below), the coordination between a ligand and a metal is through the nitrogen atom of the cyanogroup. This is in agreement with the fact that our attempts to involve α,β-unsaturated ketones **1a—b** in the reaction with $Re_2(CO)_{10}$ failed. In the reactions of **1c** with $Re_2(CO)_{10}$, disubstituted complexes $Re_2(CO)_8(ArCOCH{=}CHCN)_2$ are formed in trace amounts.

It should be pointed out that mono- and disubstituted complexes of Mn and Re with the simplest nitriles have been reported in the literature.[4,5]

Complexes **2a,b** were isolated as dark red oily substances, and complexes **2c,d** were isolated as dark red crystals. Rhenium complexes **2c,d** are more stable in solution than their manganese analogs **2a,b**.

It was possible to record the ^1H NMR spectra for complexes **2c,d**. The olefin protons give two doublets with chemical shifts at 6.81 and 7.82 ppm for **2c** and

$$M_2(CO)_{10} + RCOCH{=}CHCN \xrightarrow[Me_3NO]{} M_2(CO)_9RCOCH{=}CHCN \quad (1)$$

M = Mn, Re

2a—d
a: R = Ph, M = Mn
b: R = *o*-ClC_6H_4, M = Mn
c: R = Ph, M = Re
d: R = *o*-ClC_6H_4, M = Re

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6.67 and 7.56 ppm for **2d**, respectively; in both cases the coupling constants are 16 Hz. These data attest that the olefin bond remains uncoordinated, and the ligand retains the initial *trans*-configuration. In the ^{13}C NMR spectrum of complex **2c**, the carbonylmetal groups appear as three narrow signals at 198.91, 192.67, and 185.07 ppm and one broad signal at 195.25 ppm. Analogous data have been obtained earlier for $Re_2(CO)_9(CH_3CN)$.[5] The signal at 184.91 ppm can be assigned to the uncoordinated ketone group of the ligand. The signals at 143.66 and 108.73 ppm are assigned to the carbon atoms of the uncoordinated olefin bond. The fact that the signal for the cyanogroup in **2c** (126 ppm) is shifted down-field 10 ppm relative to the free ligand indicates the coordination of the metal with the nitrogen atom and is in agreement with the literature data.[5]

In the IR spectra of compounds **2a—d**, six absorption bands for the CO ligands are observed at 2100—1940 cm^{-1}.

If the obtained spectral data are compared with the literature data,[4—6] it is possible to conclude that complexes **2a—d** exist as the equatorial isomers (C_s-symmetry).*

Attempts to obtain disubstituted derivatives $Re_2(CO)_8(ArCOCH{=}CHCN)_2$ in a good yield by the direct interaction of $Re_2(CO)_{10}$ with excess **1c,d** and Me_3NO were unsuccessful. However, it was possible to synthesize complex **3** in 63 % yield by the interaction between complex **2c** and equimolar amounts of **1c** and Me_3NO (Eq. (2)).

$$\underset{\mathbf{2c}}{Re_2(CO)_9PhCOCH{=}CHCN} + \underset{\mathbf{1c}}{PhCOCH{=}CHCN} \xrightarrow[Me_3NO]{}$$

$$\rightarrow \underset{\mathbf{3}}{Re_2(CO)_8(PhCOCH{=}CHCN)_2} \qquad (2)$$

According to the IR spectral data, **3** has the *eq,eq*-structure.[5,8]

To synthesize heteronuclear complexes, we also made an attempt to use compounds **2c,d**, which contain a free enone system that, as a rule, is active in reactions with iron carbonyls.[8] However, of the products of the reaction of **2c,d** with $Fe_2(CO)_9$, only $Re_2(CO)_{10}$ was capable of isolation. It seems likely that the ligand—metal bond in **2c,d** is weak, and the ligand can easily lose the carbonylrhenium group. As is known, when liberated, **1c,d** does not form stable complexes with iron carbonyls.[10]

Experimental

^1H NMR ($CDCl_3$, δ) and ^{13}C ($CDCl_3$, δ) spectra were measured on a Bruker WP-200SY instrument.

IR spectra (heptane, ν/cm^{-1}) were recorded on a Specord IR-75 spectrophotometer, and *trans*-1-Aryl-3-cyanoprop-2-en-1-ones were synthesized by the described procedure.[11]

***eq*-(3-Cyano-1-phenyl-prop-2-en-1-on)nonacarbonyldirhenium (2c).** A solution of 150 mg (2 mmol) of Me_3NO in 20 mL of CH_2Cl_2 was added dropwise to a solution of 652 mg (1 mmol) of $Re_2(CO)_{10}$ and 314 mg (2 mmol) of **1c** in 80 mL of CH_2Cl_2 at ~20 °C. After 5 h, the solvent was removed from the reaction mixture *in vacuo*. The residue was chromatographed on silica gel. Unreacted $Re_2(CO)_{10}$ (62 mg, ~10 %) was eluted with heptane. Then, **2c** (388 mg, 54 %) was eluted with a heptane—CH_2Cl_2 (10 : 1) mixture. M.p. 129 °C. Found (%): C, 29.46; H, 0.98; Re 47.32. $C_{19}H_7NO_{10}Re_2$. Calculated (%): C, 29.19; H, 0.91; Re, 47.64. ^1H NMR ($CDCl_3$), δ: 6.81 (d, CH=, *J* = 16.0 Hz); 7.82 (d, CH=, *J* = 16.0 Hz); 7.54—7.96 (m, C_6H_5). ^{13}C NMR ($CDCl_3$), δ: 198.91, 195.25, 192.67, 185.07 (C≡O), 184.91 (C=O), 143.66, 108.73 (C=C), 126.25 (C≡N), 128.82, 129.21, 134.85, 135.09 (C_6H_5). IR (heptane, ν/cm^{-1}): 2098, 2045, 2020, 1990, 1964, 1944 (CO), 1675 (C=O).

***eq*-(3-Cyano-1-phenyl-prop-2-en-1-on)nonacarbonyldimanganese (2a).** A solution of 150 mg (2 mmol) of Me_3NO in 15 mL of CH_2Cl_2 was added to a solution of 390 mg (1 mmol) of $Mn_2(CO)_{10}$ and 314 mg (2 mmol) of **1c** in 100 mL of CH_2Cl_2 at ~20 °C. The reaction mixture was treated according to the procedure described above. Unreacted $Mn_2(CO)_{10}$ (45 mg, 12 %) was isolated. Then, **2a** (183 mg, 40 %) was eluted with a heptane—CH_2Cl_2 (5 : 1) mixture. M.p. 86 °C. Found (%): C, 43.73; H, 1.65; Mn, 21.35. $C_{19}H_7Mn_2NO_{10}$. Calculated (%): C, 43.95; H, 1.36; Mn, 21.19. IR: 2086, 2024, 2002, 1992, 1964, 1944 (C≡O), 1674 (C=O).

***eq*-(1-*o*-Chlorophenyl-3-cyanoprop-2-en-1-on)dimanganese nonacarbonyl (2b).** A solution of 75 mg (1 mmol) of Me_3NO in 10 mL of CH_2Cl_2 was added dropwise to a solution of 195 mg (0.5 mmol) of $Mn_2(CO)_{10}$ and 191.5 mg (1 mmol) of **1b** in 50 mL of CH_2Cl_2 at ~20 °C. After 3 h, the solvent was removed *in vacuo*. The residue was chromatographed on silica gel with heptane as the eluent, and the unreacted $Mn_2(CO)_{10}$ (18 mg, 9 %) was isolated. Then, **2b** (87.2 mg, 37 %) was eluted with a heptane—CH_2Cl_2 (5 : 1) mixture. IR: 2084, 2024, 2002, 1990, 1964, 1950 (CO); 1676 (C=O).

***eq*-(1-*o*-Chlorophenyl-3-cyanoprop-2-en-1-on)dirhenium nonacarbonyl (2d).** A solution of 150 mg (2 mmol) of Me_3NO in 20 mL of CH_2Cl_2 was added dropwise to a solution of 652 mg (1 mmol) of $Re_2(CO)_{10}$ and 383 mg (2 mmol) of **1d** in 80 mL of CH_2Cl_2 at ~20 °C. The reaction mixture was treated as in the pervious experiment. Compound **2d** (391 mg, 38 %) was isolated. ^1H NMR ($CDCl_3$), δ: 6.67 (d, CH=, *J* = 16.0 Hz); 7.56 (d, CH=, *J* = 15.97 Hz); 7.48—7.58 (m, C_6H_4). IR: 2098, 2044, 2010, 1990, 1964, 1944 (C≡O); 1675 (C=O).

***eq,eq*-Bis(3-Cyano-1-phenyl-prop-2-en-1-on)octacarbonyldirhenium (3).** A solution of 7.5 mg (0.1 mmol) of Me_3NO in 3 mL of CH_2Cl_2 was added dropwise to a solution of 78 mg (0.1 mmol) of **2c** and 15.7 mg (0.1 mmol) of **1c** in 30 mL of CH_2Cl_2 at ~20 °C. When the reaction was finished, the solvent was removed *in vacuo*. The residue was chromatographed on silica gel. Compound **3** (57.3 mg, 63 %) was eluted with chloroform. Decomposition temperature 195 °C. Found (%): C, 36.76; H, 1.78; Re, 40.83. $C_{28}H_{14}N_2O_{10}Re_2$. Calculated

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* Concerning the axial and equatorial Mn and Re derivatives see Ref. 7.

(%): C, 36.91; H, 1.54; Re, 40.91. IR ($CHCl_3$): 2064, 2018, 1968, 1908 (CO); 1660 (C=O).

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