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Preliminary communication

Design, synthesis and heterotrimetallic complexes of functionalized tweezer ligands

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Abstract

The tweezer molecules pyridine-2,6-[o-$CH_2XC_6H_5(CH_3)(Cr(CO)_3)]_2$ and 1,10-phenanthroline-2,9-[o-$CH_2XC_6H_5(CH_3)(Cr(CO)_3)]_2$ ($X = NH$, OCH_2, SCH_2) have been synthesized, and their trinuclear dichromium(0)-rhodium(I) derivatives shown to undergo fast thermal and photochemical carbonyl exchanges.

Nitrogen ligands such as pyridine, 2,2′-bipyridine and 1,10-phenanthroline (phen) coordinated to transition metals have been studied extensively, and it has been demonstrated that many complexes exhibit well-defined photochemical, electrochemical and catalytic properties [1]. Of specific interest to us was the possibility of combining within the same molecule an arenemetal complex and a heterocyclic α-diimine ligand, in order to complex a third metal and to study, the ligand exchange reactions. We report here the synthesis of a new family of ligands which combine a pyridine or a phenanthroline with two arenechromium tricarbonyl complexes, as well as the preparation of the corresponding trinuclear dichromium(0)-rhodium(I) complexes. We have also demonstrated the thermal and photochemical lability of the coordinated carbonyls.

Reaction of (o-toluidine)chromium tricarbonyl [2] with pyridine-2,6-dicarboxaldehyde [3*] or 1,10-phenanthroline-2,9-dicarboxaldehyde [4] in the presence of a catalytic amount of p-toluenesulfonic acid in refluxing benzene gave the corresponding diimines, which were isolated as deep red complexes: **1** (80%; the FAB mass spectrum contained a peak at (m/z 586, $[M+H]^+$) and **2** (82% m/z 687, $[M+H]^+$). Reduction with excess $NaBH_4$ in THF afforded the pale yellow

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* Reference number with asterisk indicates a note in the list of references.

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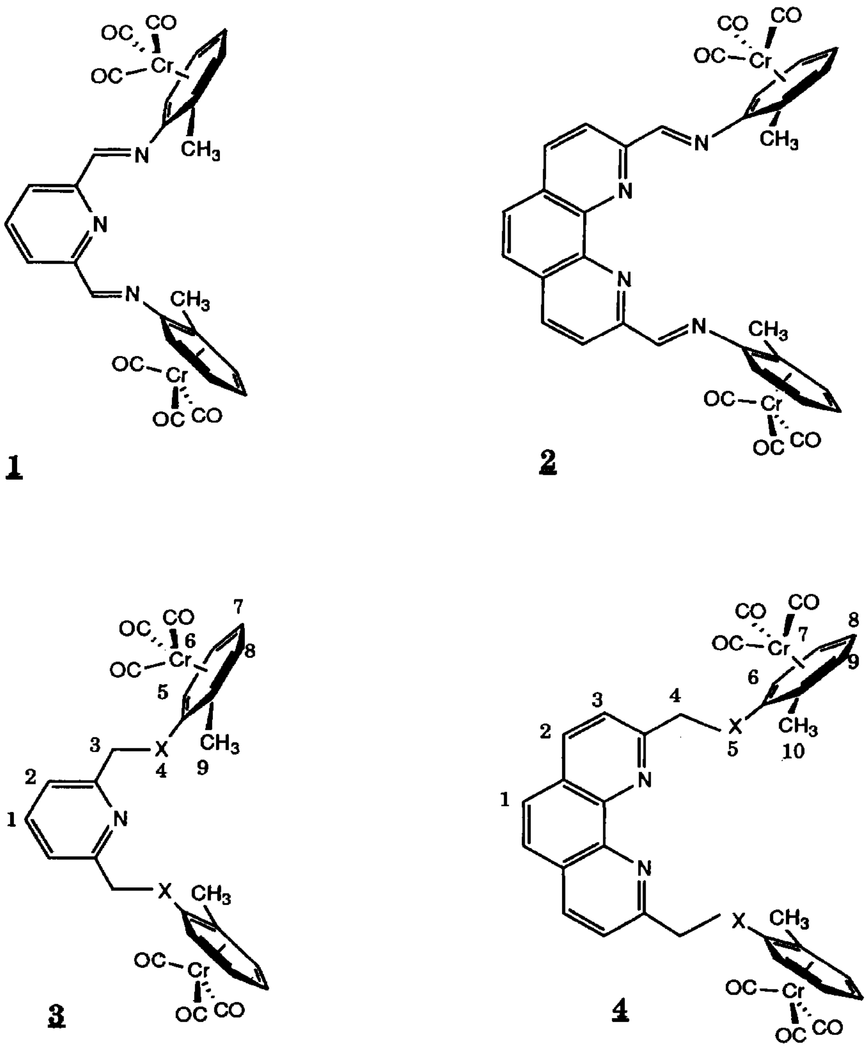
diamines: **3a** (80%; m/z 590, $[M+H]^+$) and **4a** (70%; m/z 691, $[M+H]^+$) for proton and carbon spectra see Table 1.

Reaction of the sodium salt of (o-methylbenzylalcohol)chromiumtricarbonyl [5*] or the sodium salt of (o-methylbenzylthioalcohol)chromiumtricarbonyl [6*] with 2,6-bis(bromomethyl)pyridine [7] or 2,9-bis(bromomethyl)-1,10-phenanthroline [4] in THF gave the diethers **3b** (96%; m/z 620, $[M+H]^+$) and **4b** (40%; m/z 721, $[M+H]^+$) as yellow oils, and the disulfides **3c** (89%; m/z 652, $[M+H]^+$) and **4c** (70%; m/z 753, $[M+H]^+$) as deep yellow oils (Scheme 1).



a ; X = NH

b ; X = OCH_2

c ; X = SCH_2

a ; X = NH

b ; X = OCH_2

c ; X = SCH_2

Scheme 1. Schematic representation of ligands synthesized as diastereomeric mixtures. For clarity only one enantiomer of the d,l isomer mixture is shown.

Table 1

Selected data for compounds **3**, **4**, **5a** and **6a** (*meso, d,l*). ^{1}H NMR spectra: 200 MHz acetone-d_6; ^{13}C NMR spectra: 100 MHz acetone-d_6; IR spectra; acetone

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3: IR: ν 3380 (m, NH), 1955, 1865 (vs,CO,Cr), 1550 (m), 1300 (m) cm^{-1}; ^{1}H NMR: δ 7.95 (*t*, $J_{1,2}$ 7.7 Hz, 1H, H-1), 7.55 (d, $J_{2,1}$ 7.7 Hz, 2H, H-2), 6.09 (m, 2H, H-4), 5.98 (d, $J_{5,6}$ 6.3 Hz, 2H, H-5), 5.76 (t, $J_{7,6} = J_{7,8} = 6.3$ Hz, 2H, H-7), 5.25 (d, $J_{8,7}$ 6.3 Hz, 2H, H-8), 5.16(t, $J_{6,7} = J_{6,5} = 6.3$ Hz, 2H, H-6), 4.63 (d, $J_{3,4}$ 5.2 Hz, 4H, H-3); ^{13}C NMR: δ 236.75, 157.86, 138.93, 134.04, 133.99, 121.75, 100.74, 97.33, 93.87, 85.54, 85.51, 76.30, 76.26, 49.36, 17.99 ppm

4: IR: ν 3380 (m, NH), 1950, 1865 (vs, CO,Cr), cm^{-1}; ^{1}H NMR: δ 8.64 (d, $J_{2,3}$ 8.4 Hz; 2H, H-2), 8.14 (s, 2H, H-1), 8.02 (d, $J_{3,2}$ 8.4 Hz, 2H, H-3), 6.84 (m, 2H, H-5), 6.02 (m, 2H, H-6), 5.80 (m, 2H, H-8), 5.41 (d, $J_{9,8}$ 6.9 Hz, 2H, H-9), 5.16 (m, 2H, H-7), 4.95 (m, 4H, H-5), 2.60 (s, 3H, H-10), 2.59 (s, 3H, H-10); ^{13}C NMR: δ 236.99, 158.66, 145.96, 138.50, 134.53, 134.40, 129.56, 127.86, 123.03, 101.22, 101.50, 97.90, 97.57, 94.39, 94.03, 85.79, 85.84, 76.59, 76.27, 50.37, 18.41 ppm

5a: IR: ν 3380 (m, NH), 2060, 1985 (m, CO, Rh), 1950, 1865 (vs, CO, Cr), 315 (m, Rh-Cl) cm^{-1}; ^{1}H NMR δ 8.26 (t, $J_{1,2}$ 7.5 Hz, 1H, H-1), 7.91 (d, $J_{2,1}$ 7.5 Hz, 1H, H-2), 6.25 (m, 2H, H-4), 5.97 (d, J(5,6) = 6.2 Hz, 2H, H-5), 5.70 (m, 2H, H-7), 520–5.40 (m, 8H, H-3,6,8), 2.44 (s, 6H, H-9); ^{13}C NMR: δ 236.62, 161.77, 142.12, 132.50, 132.41, 124.46, 100.13, 100.05, 96.58, 96.52, 94.74, 86.92, 86.86, 77.48, 51.98, 18.14 ppm

6a: IR: ν 3380 (m, NH), 2055, 1980 (m, CO, Rh), 1950, 1865 (vs, CO, Cr) cm^{-1}; ^{1}H NMR δ 8.93 (d, $J_{2,3}$ 8.3 Hz, 2H, H-2), 8.40 (d, $J_{3,2}$ 8.3 Hz, 2H, H-3), 8.33 (s, 2H, H-1), 6.48 (m, 2H, H-5), 5.96 (d, J 6.2 Hz, 2H, H-6), 5.8–5.2 (m, 10H, H-4,7,8,9), 2.50 (broad s, 6H, H-10); ^{13}C NMR: δ 236.69, 173.58, 169.72, 140.37, 138.40, 130.58, 128.01, 124.73, 100.35, 99.71, 97.57, 97.04, 96.61, 96.18, 87.08, 86.15, 77.84, 77.55, 54.23, 53.75, 18.25 ppm

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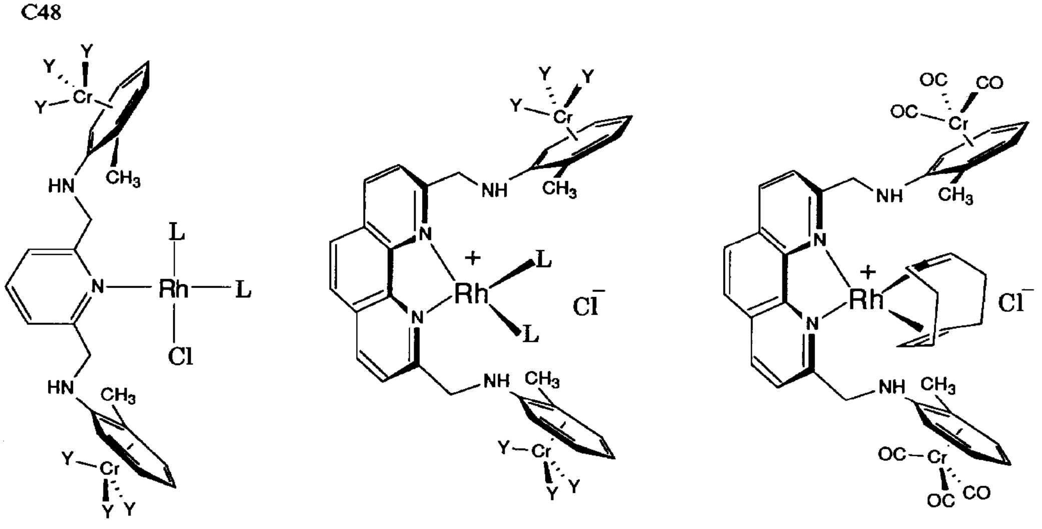
These new ligands were used to synthesize square planar rhodium(I) complexes. Reaction of 0.5 equiv. of chlorodicarbonylrhodium(I) dimer with ligand **3a** in CH_2Cl_2 produced, on addition of pentane, a yellow solid (complex **5a**, 47%). The ^{1}H NMR spectrum showed a 0.36 ppm downfield shift for the two types of pyridine protons, and there was no change in the NH vibration in the IR spectrum (see Table 1). The FAB spectrum showed a molecular ion peak at m/z 782.9 (M^+) with an isotope pattern characteristic of the presence of chloride, and loss of the chloride ion at m/z 747.9 ($[M - Cl]^+$). These observations suggest that the rhodium(I) is coordinated only by the pyridine nitrogen, one CO being *trans* to the pyridine and the other *trans* to Cl, by analogy with the known $C_5H_5NRh(CO)_2Cl$ complex [8]. In contrast, reaction of **4a** with 0.5 equiv. of chlorodicarbonylrhodium(I) dimer in CH_2Cl_2 gave a yellow precipitate that proved to be the cationic complex **6a** (60%; m/z 849, $[M]^+$). This complex has an infrared spectrum similar to the described $[(phen)Rh(CO)_2]^+$ species [9]. Reaction of 0.5 equiv. of chloro (1,5-cyclooctadiene)-rhodium(I) dimer with **4a** in CH_2Cl_2 gave, on addition of pentane, a deep yellow solid (complex **7**; 57%; m/z 901, M^+) (Scheme 2).

We have not made detailed studies of the thermal or photochemical substitution of carbonyls with labelled carbon monoxide in the case of the arenechromium complexes, but did examine $^{13}CO/CO$ ligand exchange reactions in the case of the ligands **3a**, **4a** and the complexes **5**, **6** by ^{13}C NMR and IR spectroscopy. When $[Rh(^{13}CO)_2Cl]_2$ (ca. 90% enriched) [10] was used to complex ligand **3a**, no labelled carbonyls coordinated to the rhodium could be detected by ^{13}C NMR and IR spectroscopy, but carbonyl exchange on the arenechromium tricarbonyl was observed (singlet at 236.6 ppm). Furthermore no complexation occurred when (*o*-



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a ; Y = L = CO

b ; Y = CO L = ^{13}CO

c ; Y = L = ^{13}CO

6

a ; Y = L = CO

b ; Y = CO L = ^{13}CO

c ; Y = L = ^{13}CO

7

Scheme 2. Schematic representation of complexes prepared as diastereomeric mixtures.

toluidine)chromium tricarbonyl (2 equiv.) reacted with the labelled rhodium dimer (0.5 equiv.), and only carbonyl exchange on the arenechromium tricarbonyl was observed (singlet at 235.0 ppm). When ligand **4a** was used, no chromium–carbonyl exchange was detected and complex **6b** was formed [11*]. This behaviour may be due to the preformation of a bridged chromium(0)-rhodium(I) dimeric species which can undergo carbonyl exchange to the arenechromium and the formation of a thermodynamic product with the rhodium coordinated to the pyridine. In the case of (*o*-toluidine)chromium tricarbonyl no complexation occurred because of the weak basicity of the amino group [12]. In contrast, the chelating properties of the phenanthroline subunit favours the formation of a kinetic product without exchange of the chromium carbonyls.

When complexes **5a** and **6a** were kept under a labelled carbon monoxide atmosphere (90.5% enriched) for several hours, in the dark only carbonyl exchange on rhodium was observed, and complexes **5b** and **6b** were isolated [11]. However, brief photolysis of complexes **5b** or **6b** under ^{13}CO in sealed NMR tubes resulted in fast exchange of all the carbonyls (Scheme 2). The presence of rhodium is not needed for the chromium-carbonyl exchange, because rapid labelling of the ligands is observed under identical photolysis conditions (singlet at 236.8 ppm, $\nu(^{13}\text{CO,Cr})$ 1905, 1820cm^{-1} for **3a** and singlet at 236.7 ppm, $\nu(^{13}\text{CO,Cr})$ 1910, 1830 cm^{-1} for **4a**). Irradiation of complexes **5c** and **6c** for longer times resulted in a colour change from yellow to deep-red, with formation of a new rhodium complex in the case of the phenanthroline ligand **4a** (singlet at 236.6 ppm (CO,Cr); doublet at 187.8 ppm, J(Rh,C) 74 Hz) and of $\text{Cr}(^{13}\text{CO})_6$ (singlet at 213.3 ppm and ν(CO) 1935 cm^{-1}). Labelled hexacarbonylchromium is formed by decomplexation of the arene-chromium complex, followed by trapping of $\text{Cr}(^{13}\text{CO})_3(\text{solvent})_3$ by the excess of ^{13}CO.

The unstable rhodium complex could be formed by coordination of one amino group to the rhodium(I) centre. Work in progress is aimed at isolation of this species and synthesis of optically pure ligands by the use of chiral arenechromium tribarbonyl complexes [13] as well as the macrocyclic analogues.

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