Syntheses and Structures of Transition-Metal Complexes of Mesoionic Olate, Thiolate, Selenolate, and Cyclopentadienide

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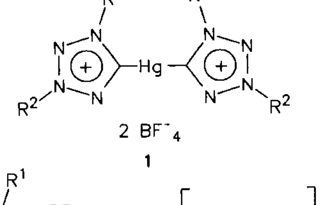
The dicarbonyl(η-cyclopentadienyl)iron(II) complex **5** of 1,3-diphenyltetrazolium-5-olate (**4**) and the pentacarbonylmolybdenum(0) complexes **7**, **11**, and **9** of 1,3-diphenyltetrazolium-5-thiolate (**6**), -5-selenolate (**10**), and 5-methyl-1,4-diphenyl-1,2,4-triazolium-3-thiolate (**8**) as well as tricarbonylchromium(0) complex **13** and -molybdenum(0) complex **14** of 1,3-diphenyltetrazolium-5-cyclopentadienide (**12**) have been prepared. Their physicochemical properties are discussed on the basis of spectroscopic properties.

In the preceding paper[1] we have described the first synthesis of cationic mercury(II) (**1**) and palladium(II) complexes (**2**) which may be regarded as mesoion-derived carbene complexes. Apart from this novel type of organometallic compounds, transition metal complexes **3** of mesoions constitute another type of mesoion-related organometallic heterocycles. Mesoionic compounds appear to offer a variety of coordination sites (e.g. heterocyclic ring and exocyclic atom), and several kinds of coordination modes (e.g. σ and π bonding) can be expected. In such complexes, electronic states of the ligands are considered to be perturbed by complexation compared with those of free mesoions. It is then interesting to study the properties of the mesoions coordinated to transition metals. However, such compounds have received very scarce attention so far. This paper describes the first synthesis as well as some spectroscopic properties of metal carbonyl complexes of mesoionic olate, thiolate, selenolate, and cyclopentadienide.



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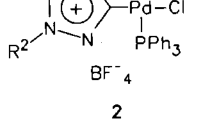

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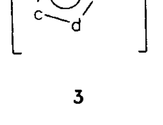

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Results and Discussion

1,3-Diphenyltetrazolium-5-olate (**4**) is ultrasonicated with dicarbonyl(η-cyclopentadienyl)iodoiron(II) in the presence of silver tetrafluoroborate in dichloromethane for 1 h. Recrystallization gives yellow crystals of a cationic iron(II) complex **5** (Eq. 1). The infrared spectrum shows the carbonyl stretching vibrations at 2075 and 2010 cm^{-1}. These frequencies are similar to those of known CpFe(CO)$_2$(ketone)$^+$ complexes[2]. The intense absorption at 1720 cm^{-1} is attributed to the tetrazolium carbon–oxygen stretching mode ν(C–O)[3], and this value is shifted to higher wavelength compared with that of free **4** (1695 cm^{-1}). This fact contrasts to the cases of simple ketones[2a] such as acetone and of polar ketones[2b] such as tropone, in which carbonyl stretching frequencies are decreased upon complexation. The ^{13}C-NMR chemical shift of the tetrazolium ring carbon of **5** is 161.4, comparable to that of 5-ethoxy-1,3-diphenyltetrazolium ($\delta = 160.7$), suggesting that the iron atom of **5** is σ-bound to the exocyclic oxygen atom.

An attempt to obtain a similar iron complex of 1,3-diphenyltetrazolium-5-thiolate (**6**) has failed. However, heating **6** with hexacarbonylmolybdenum in benzene (80°C, 1.5 h) gives a high yield of a neutral pentacarbonylmolybdenum(0) complex **7** as stable dark red crystals (Eq. 2). The mass spectrum has not provided useful information owing to the poor volatility of **7**, but the structure of this compound is supported by elemental analysis and spectroscopic data. The IR spectrum reveals intense carbonyl stretching absorptions at 2080, 1940, and 1892 cm^{-1}, assignable to A$_1$(2), E, and A$_1$(1) modes, respectively, characteristic of pentacarbonylmolybdenum(0) complexes with C_{4v} symmetry[4]. The wavenumbers are similar to those of pentacarbonylmolybdenum complexes of thio ethers[5]. An increase in the tetrazolium carbon-sulfur stretching frequency ν(C–S) caused by coordination from 1370 to 1386 cm^{-1} is observed also for this complex. The ^{1}H- and ^{13}C-NMR chemical shifts of **7** are very similar to those of free **6**, indicating that the molybdenum atom coordinates to the sulfur of thiolates **6**. The use of hexacarbonylchromium in place of hexacarbonyl-

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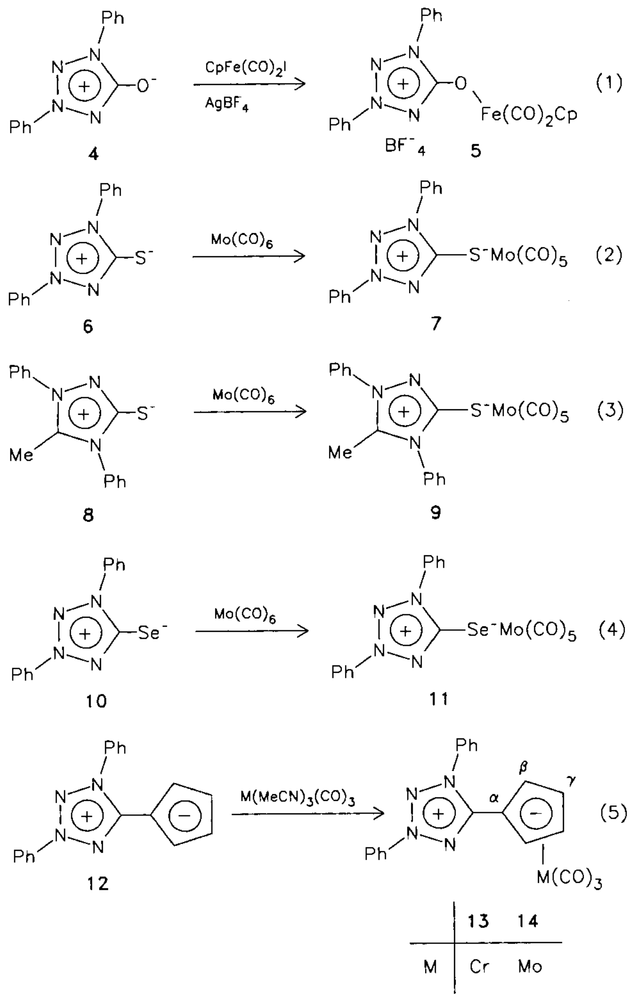
molybdenum does not give the corresponding chromium complex even under rigorous reaction conditions (refluxing toluene, 2 h). The reaction of 5-methyl-1,4-diphenyl-1,2,4-triazolium-3-thiolate (**8**) with hexacarbonylmolybdenum gives a similar pentacarbonylmolybdenum(0) complex **9** (Eq. 3).



1,3-Diphenyltetrazolium-5-selenolate (**10**) also provides a stable molybdenum(0) complex (**11**) upon treatment with hexacarbonylmolybdenum, though the yield is only modest (10%) (Eq. 4). Again, the spectroscopic data indicate that **11** is a pentacarbonyl complex similar to **7**. In addition to three strong bands (two A_1 and one E), a weak B_1 absorption (IR-forbidden) was observed at 1982 cm^{-1} in the IR spectrum. This compound represents a rare example of pentacarbonylmolybdenum(0) complexes of selenocarbonyl compounds.

1,3-Diphenyltetrazolium-5-cyclopentadienide (**12**) is a unique mesoionic compound possessing an unsubstituted cyclopentadienide ring and can be best described by a dipolar tetrazolium-cyclopentadienide structure[6]. Heating of **12** with tris(acetonitrile)tricarbonylchromium(0) in benzene gives a stable tricarbonylchromium(0) complex **13** (Eq. 5). A similar reaction with tris(acetonitrile)tricarbonylmolybdenum(0) yields the corresponding molybdenum(0) complex **14**. Chromium (**13**) and molybdenum complexes (**14**) are air-stable in crystalline form, but in solutions they rapidly decompose on contact with air to liberate the ligand **12**. The ^{1}H- and ^{13}C-NMR spectral data of **13** and **14** are listed in Table 1 together with those of the ligand **12** for comparison purposes. The cyclopentadienide ring protons of **13** and **14** resonate at higher magnetic field by 0.42 – 1.06 ppm than those of **12**. The ^{13}C-NMR chemical shifts of the cyclopentadienyl carbons show similar high-field shifts (20 – 29 ppm) due to complexation, whereas the tetrazolium ring carbon of **12**–**14** is registered at almost coincident position. These facts indicate that the tricarbonylmetal tripods of **13** and **14** coordinate to the electron-rich cyclopentadienyl ring, and the compounds **13** and **14** can be regarded as tetrazolium-cation substituted tricarbonyl(η-cyclopentadienyl)chromium(0) and -molybdenum(0) complexes, respectively. In the IR spectra, the stretching vibrations of the pivotal carbon bond of **13** (1548 cm^{-1}) and **14** (1546 cm^{-1}) are shifted to lower wavelength compared with that of free **12** (1561 cm^{-1}), indicating that the double-bond character of this bond is decreased and hence the contribution of the polar tetrazolium-cyclopentadienide structure is increased by complexation[7].

Table 1. ^{1}H- (200 MHz, [D$_6$]DMSO) and ^{13}C-NMR data (50 MHz, [D$_6$]DMSO) of mesoion **12** and its tricarbonylchromium **13** and tricarbonylmolybdenum complexes **14** (δ values)

12	13	14
^{1}H NMR		
5.81 (m, 4H, Cp)	4.75 (m, 4H, Cp)	5.39 (m, 4H, Cp)
7.80 (m, 8H, Ph)	7.87 (m, 8H, Ph)	7.98 (m, 8H, Ph)
8.20 (m, 2H, Ph)	8.24 (m, 2H, Ph)	8.35 (m, 2H, Ph)
^{13}C NMR		
96.6 (C-α)	70.6 (C-α)	76.9 (C-α)
111.9 114.4 (C-β, γ)	85.4 (C-β and C-γ)	90.1 90.2 (C-β, γ)
120.8 (C-*o*)	121.3 (C-*o*)	121.3 (C-*o*)
127.5 (C-*o*)	127.2 (C-*o*)	127.1 (C-*o*)
130.3 (C-*m*)	130.4 (C-*m*)	130.5 (C-*m*)
130.4 (C-*m*)	130.7 (C-*m*)	130.7 (C-*m*)
131.9 (C-*p*)	133.2 (C-*p*)	133.3 (C-*p*)
132.4 (C-*p*)	133.4 (C-*p*)	133.4 (C-*p*)
134.5 (C-*i*)	132.1 (C-*i*)	132.3 (C-*i*)
135.7 (C-*i*)	134.7 (C-*i*)	134.8 (C-*i*)
159.0 (C$^+$)	160.5 (C$^+$)	159.0 (C$^+$)
	241.4 (CO)	231.3 (CO)

In conclusion, six transition metal complexes of mesoionic compounds have been synthesized, and it has been found that the metals coordinate to the electron-rich exocyclic group (f) of mesoions regardless of the kind of the metal and exocyclic atom.

Experimental

General: See preceding paper[1].

Dicarbonyl(η-cyclopentadienyl)iron(II) Complex **5** *of 1,3-Diphenyltetrazolium-5-olate* (**4**): A mixture of dicarbonyl(η-cyclopentadienyl)iodoiron(II) (205 mg, 0.67 mmol), olate **4** (238 mg, 1.0

mmol), and silver tetrafluoroborate (142 mg, 0.73 mmol) in dichloromethane (15 ml) was ultrasonicated at room temp. for 1 h. The mixture was filtered and the solvent evaporated. The residue was reprecipitated twice from dichloromethane/ether and finally recrystallized from acetonitrile/ether to give **5**; 130 mg (39%) as yellow crystals, m.p. 149 °C (dec.). – IR (KBr): $\tilde{\nu} = 2070\ \mathrm{cm^{-1}}$ (CO), 2010 (CO), 1720 (C–O), 1492, 1390, 1100–1000, 780, 764, 692. – UV (MeCN): λ_{max} (log ε) = 220 nm (sh, 4.31), 270 (3.95), 317 (4.01). – ^{1}H NMR (90 MHz, CD_3CN): δ = 5.34 (s, 5H, Cp), 7.6–8.0 (m, 10H, Ph). – ^{13}C NMR (50 MHz, CD_3CN): δ = 87.6 (Cp), 122.3 (C-*o*), 128.0 (C-*o*), 130.9 (C-*m*), 131.6 (C-*m*), 131.1 (C-*p*), 134.0 (C-*i*), 134.8 (C-*p*), 136.5 (C-*i*), 161.4 (C^+), 209.9 (CO).

$C_{20}H_{15}BF_4FeN_4O_3$ (502.0)
Calcd. C 47.85 H 3.01 N 11.16
Found C 47.77 H 2.82 N 11.38

Pentacarbonylmolybdenum(0) Complex **7** *of 1,3-Diphenyltetrazolium-5-thiolate* (**6**): Thiolate **6** (25 mg, 0.10 mmol) and hexacarbonylmolybdenum (26 mg, 0.10 mmol) were gently refluxed in benzene (3 ml) for 1.5 h. The colour of the reaction mixture turned from yellow to dark red. The mixture was cooled to room temp. and then subjected to silica gel column chromatography. By rapid elution with benzene a dark red band developed. Evaporation of the solvent gave the molybdenum complex **7**; 48 mg (98%) as dark red crystals, m.p. 114 °C (dec.). – IR (KBr): $\tilde{\nu} = 2080\ \mathrm{cm^{-1}}$ (CO), 1940 (CO), 1892 (CO), 1492, 1386 (C–S), 1304, 1270, 1182, 760. – UV (MeCN): λ_{max} (log ε) = 228 nm (4.13), 251 (4.20), 376 (3.08). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.62 (m, 6H, Ph), 7.94 (m, 2H, Ph), 8.17 (m, 2H, Ph). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 120.3 (C-*o*), 124.5 (C-*o*), 129.7 (C-*m*), 130.4 (C-*m*), 131.5 (C-*p*), 132.9 (C-*p*), 133.0 (C-*i*), 135.1 (C-*i*), 173.5 (C^+), 205.6 (CO), 213.9 (CO).

$C_{18}H_{10}MoN_4O_5S$ (490.3)
Calcd. C 44.09 H 2.06 N 11.43
Found C 44.58 H 2.04 N 11.62

Pentacarbonylmolybdenum(0) Complex **9** *of 5-Methyl-1,4-diphenyl-1,2,4-triazolium-3-thiolate* (**8**) was similarly prepared as **7** from **8**[8] (27 mg, 0.10 mmol). Recrystallization from acetone/ether gave **9**; 28 mg (56%) as pale yellow crystals, m.p. 183 °C (dec.). – IR (KBr): $\tilde{\nu} = 2070\ \mathrm{cm^{-1}}$ (CO), 1932 (CO), 1916 (CO), 1854 (CO), 1518, 1350 (C–S), 1212, 770, 742, 690. – UV (MeCN): λ_{max} (log ε) = 223 nm (4.70), 247 (sh, 4.66), 368 (3.29), 397 (sh, 3.13). – ^{1}H NMR (200 MHz, [D_6]DMSO): δ = 2.37 (s, 3H, Me), 7.70 (m, 10H, Ph).

$C_{20}H_{13}MoN_3O_5S$ (503.3)
Calcd. C 47.73 H 2.60 N 8.53
Found C 47.91 H 2.67 N 8.23

Pentacarbonylmolybdenum(0) Complex **11** *of 1,3-Diphenyltetrazolium-5-selenolate* (**10**): Selenolate[1] **10** (210 mg, 0.70 mmol) and hexacarbonylmolybdenum (182 mg, 0.70 mmol) were gently refluxed in benzene (5 ml) for 30 min. The reaction mixture was subjected to silica gel chromatography (eluent: benzene). From a red-brown band, molybdenum complex **11** was obtained; 38 mg (10%) as deep red-brown crystals, m.p. 120 °C (dec.) (CH_2Cl_2/hexane). – IR (KBr): $\tilde{\nu} = 2070\ \mathrm{cm^{-1}}$ (CO), 1982 (CO), 1928 (CO), 1864 (CO), 1484, 1376 (C–Se), 1262, 1160, 762, 760. – UV (MeCN): λ_{max} (log ε) = 225 (4.44), 375 (3.48). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.71 (m, 6H, Ph), 8.00 (m, 2H, Ph), 8.23 (m, 2H, Ph). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 120.5 (C-*o*), 124.9 (C-*o*), 129.9 (C-*m*), 130.5 (C-*m*), 131.9 (C-*p*), 133.1 (C-*p*), 133.5 (C-*i*), 134.9 (C-*i*), 164.6 (C^+), 206.1 (CO), 214.3 (CO). – MS (70 eV), *m/z* (%): 314 (18), 234 (47), 154 (100).

$C_{18}H_{10}MoN_4O_5Se$ (537.2)
Calcd. C 40.25 H 1.88 N 10.43
Found C 39.99 H 1.73 N 10.41

Tricarbonylchromium(0) Complex **13** *of 1,3-Diphenyltetrazolium-5-cyclopentadienide* (**12**): Mesoion **12**[6] (57 mg, 0.20 mmol) and tris(acetonitrile)tricarbonylchromium[9] (55 mg, 0.20 mmol) were gently refluxed in benzene (7 ml) for 2 h. The reaction mixture was cooled and filtered. From the filtrate, the mesoion **12** was recovered (15 mg, 26%). The residue was washed several times with acetonitrile. The washings were combined, and the solvent was evaporated to leave chromium complex **13**; 44 mg (52%) as dark brown crystals, m.p. ca. 245 °C (dec.) (MeCN). – IR (KBr): $\tilde{\nu} = 1910\ \mathrm{cm^{-1}}$ (CO), 1798 (CO), 1548, 1492, 1414, 1366, 1064, 994, 766, 690. – UV/Vis (MeCN): λ_{max} (log ε) = 220 nm (4.53), 264 (4.46), 445 (3.60). – MS (20 eV), *m/z* (%): 422 (14) [M^+], 338 (27) [$M^+ - 3$ CO], 286 (100) [$M^+ - Cr(CO)_3$].

$C_{21}H_{14}CrN_4O_3$ (422.4)
Calcd. C 59.72 H 3.34 N 13.26
Found C 59.50 H 3.10 N 13.08

Tricarbonylmolybdenum(0) Complex **14** *of 1,3-Diphenyltetrazolium-5-cyclopentadienide* (**12**): Mesoion **12** (37 mg, 0.13 mmol) and tris(acetonitrile)tricarbonylmolybdenum[9] (39 mg, 0.13 mmol) were gently refluxed in benzene (8 ml) for 15 min. The reaction mixture was cooled and filtered to give a dark brown solid of crude molybdenum complex **14**; 57 mg (95%). This compound was unstable in solutions, and attempted recrystallization caused partial demetallation. Therefore, an analytically pure sample could not be obtained; m.p. ca. 190 °C (dec.). – IR (KBr): $\tilde{\nu} = 1912\ \mathrm{cm^{-1}}$ (CO), 1794 (CO), 1546, 1490, 1410, 1362, 1060, 990, 764, 688. – UV/Vis (MeCN): λ_{max} (log ε) = 213 (4.47), 260 (4.45), 413 (3.48). – MS (20 eV), *m/z* (%): 468 (3) [M^+], 384 (2) [$M^+ - 3$ CO], 286 (29) [$M - Mo(CO)_3$].

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