Additions of Alkylidene Groups between Co and S in the Reactions of Dithiolatocobalt Complexes with Diazo Compounds

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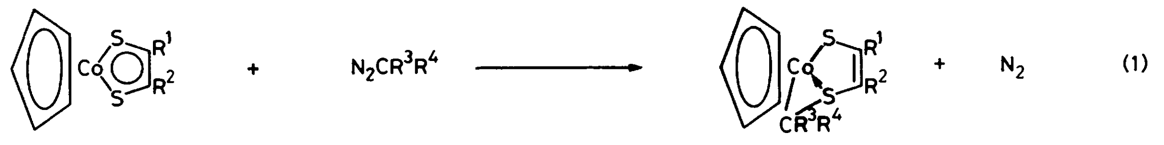
Dithiolatocobalt(III) complexes [Co(cp)(S_2C_2XY)] (**1a**; X = Y = CO_2Me) and (**1b**; X = H, Y = CO_2Me) (cp = C_5H_5) react with diazo compounds to give alkylidene adducts containing a C–Co–S three-membered ring.

There has been considerable recent interest in multiple bonds between transition metals and main group elements.[1] The metal–sulphur bond of (η-cyclopentadienyl)(ethylene-1,2-dithiolato)-cobalt(III) and -rhodium(III) complexes show several unique reactions; *e.g.* dimerization[2] and the addition of alkyne between metal and sulphur.[3] These reactions suggest that a degree of multiplicity is present in the metal–sulphur bonds of these complexes. We report here another example of addition to the metal–sulphur bond: the addition of alkylidene groups by reaction with diazo compounds.

The dithiolatocobalt(III) complexes (**1a** and **b**) reacted with diazomethane in diethyl ether–dichloromethane at 0 °C and with ethyl diazoacetate in benzene under reflux to give



(**1**)**a**; $R^1 = R^2 = CO_2Me$
b; $R^1 = H$, $R^2 = CO_2Me$

(**2**)**a**; $R^3 = R^4 = H$
b; $R^3 = H$, $R^4 = CO_2Et$
c; $R^3 = R^4 = CO_2Me$

(**3**)**a**; $R^1 = R^2 = CO_2Me$, $R^3 = R^4 = H$
b; $R^1 = R^2 = CO_2Me$, $R^3 = H$, $R^4 = CO_2Et$
c; $R^1 = R^2 = CO_2Me$, $R^3 = R^4 = CO_2Me$
d; $R^1 = H$, $R^2 = CO_2Me$, $R^3 = R^4 = H$
e; $R^1 = H$, $R^2 = CO_2Me$, $R^3 = H$, $R^4 = CO_2Et$

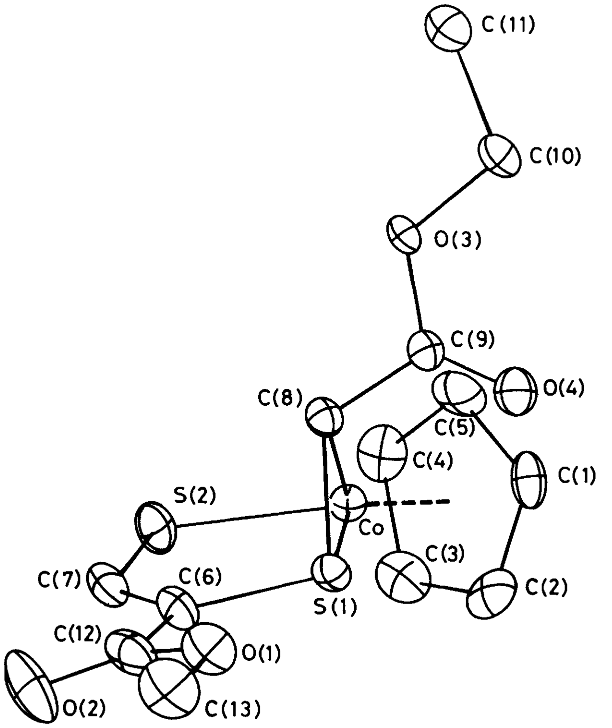


Figure 1. ORTEP drawing of adduct (**3e**). Selected bond lengths and angles: Co–S(1) 2.185(2), Co–S(2) 2.214(3), Co–C(8) 1.983(8), S(1)–C(6) 1.759(9), S(1)–C(8) 1.782(8), S(2)–C(7) 1.670(9), C(6)–C(7) 1.426(12) Å; S(1)–Co–S(2) 91.67(9), S(2)–Co–C(8) 94.02(23), S(1)–Co–C(8) 50.33(23), Co–C(8)–S(1) 70.75(28)°. The centres of the five atoms of the CoS_2C_2 moiety [Co, S(1), S(2), C(6), C(7)] are within 0.038 Å of a plane. The angle between planes η-cyclopentadienyl and CoS_2C_2 is 71.15°.

alkylidene adducts (**3a**, **b**, **d**, and **e**)† in high yields, with evolution of N_2 (equation 1). The thermal reaction of the dithiolato complex (**1a**) with dimethyl diazomalonate in benzene solution gave the adduct (**3c**) in a very low yield, whereas the addition of CuI–P(OMe)$_3$[4] to the solution raised the yield of the adduct. The results are summarized in Table 1.

Table 1. Reaction of dithiolatocobalt(III) complex (**1**) with diazo compound (**2**).

Dithiolato complex (1)	Diazo compound (2)	Reaction conditions Catalyst	Temp./°C	Time/h	Adduct (yield/%)
(**1a**)	(**2a**)	—	0	[a]	(**3a**) (92)
(**1a**)	(**2b**)	—	80	3	(**3b**) (87)
(**1a**)	(**2c**)	CuI-P(OMe)$_3$	80	12	(**3c**) (40)
(**1b**)	(**2a**)	—	0	[a]	(**3d**) (45)
(**1b**)	(**2b**)	—	80	5	(**3e**) (59)

[a] When diazomethane gas was bubbled into solutions of the dithiolatocobalt(III) complexes at 0 °C, the reaction occurred rapidly.

In order to establish the exact conformation of the adducts, the structure of (**3e**) has been determined by single crystal *X*-ray analysis.‡ The molecular structure of (**3e**) is shown in Figure 1, together with important bond parameters. The five-membered ring (dithiolene ring), which consists of Co, two S, and two C, is planar; the five-membered ring in the free dithiolato complexes is similar.[5] The plane of the C–Co–S three-membered ring is almost perpendicular to the plane of the dithiolene ring.

The bridging alkylidene group bonds to S(1) regioselectively, the adjacent ester group being oriented *exo* to the dithiolene ring.

Irradiation of a dichloromethane solution of the dithiolato complex (**1a**) and ethyl diazoacetate or dimethyl diazomalonate with a high pressure mercury lamp at room temperature brought about rapid decomposition of (**1a**) without formation of the adduct. Adduct formation was not observed on irradiation in the presence of benzophenone, a triplet sensitizer. These facts indicate that the alkylidene adduct is formed by reaction of the dithiolatocobalt(III) complex, not with the free carbene species, but with the diazo compound, followed

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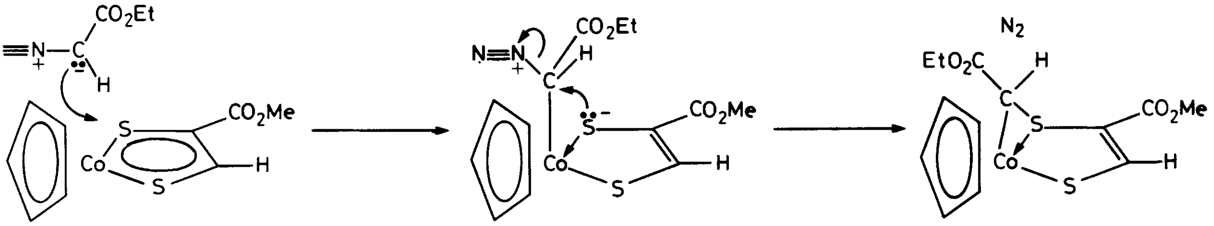
† *Physical and spectroscopic data* for (**3e**): m.p. 112 °C; IR(KBr disk) ν 1700, 1490, 1290, 1240, 1140, and 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.10 [d, $^5J_{HH}$ 0.74 Hz, 1H, H at dithiolene ring C(7)], 5.12 (s, 5H, C_5H_5), 4.22 (q, $^3J_{HH}$ 7.0 Hz, 2H, CH_2CH_3), 3.72 (s, 3H, CH_3), 2.02 [d, $^5J_{HH}$ 0.74 Hz, 1H, C(8)H], and 1.34 (t, $^3J_{HH}$ 7.0 Hz, 3H, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 84.8 (C_5H_5), 178.4, 174.0 [J_{CH} 170.9 Hz, dithiolene ring C(7)], 163.3, 116.2 [dithiolene ring C(6)], 61.1, 52.0, 34.2 [J_{CH} 175.8 Hz, C(8)], and 14.6; MS(EI, 70 eV) *m/z* 358 (M^+) (34%), 285 [$(M - CO_2Et)^+$] (79%), 272 [$(M - HCO_2Et)^+$] (20%), 188 ($CpCoS_2^+$) (100%), and 124 ($CpCo^+$) (34%).

The other new compounds also gave satisfactory elemental analyses and spectroscopic data.

‡ *Crystal data* for (**3e**): $C_{13}H_{15}CoS_2O_4$, $M = 358.30$, triclinic, space group $P\bar{1}$, $a = 9.637(3)$, $b = 10.852(2)$, $c = 7.551(3)$ Å, $\alpha = 102.51(2)$, $\beta = 106.92(4)$, $\gamma = 84.31(4)°$, $U = 736.92$ Å^3, $D_c = 1.615$ g cm^{-3}, $Z = 2$, $\lambda(\text{Mo-}K_\alpha) = 0.71073$ Å, $\mu = 14.41$ cm^{-1}. Reflection intensities were collected by the ω-scan technique ($2\theta < 60°$) on a Rigaku AFC-5 automated four-circle diffractometer. The structure was solved by the heavy atom method and refined by a block-diagonal least-squares method and only in the last cycle by a full-matrix least-squares method, which used anisotropic temperature factors for all non-hydrogen atoms, all the parameter shifts being less than one-third of the corresponding standard deviations. The weighting scale was $w = 1/(\sigma^2 F)$. Final R value 0.070 ($R_w = 0.082$) on 3321 intensities ($|F_o| > 3\sigma|F_o|$). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1

by the elimination of N_2. Adduct formation appears to proceed *via* nucleophilic attack of the diazo compounds on the dithiolato complexes: the introduction of electronegative alkylester substituents to diazomethane reduced the reactivity and that in the dithiolene ring promotes the reactivity.

In (η-cyclopentadienyl)(ethylene-1,2-dithiolato)cobalt(III), the lowest unoccupied orbital is the d orbital on the cobalt atom.[6] It has been concluded that in diazomethane the carbon atom is negatively charged and the nitrogen atoms are positively charged.[7] Thus, a mechanism for the reaction in the absence of a catalyst can be proposed as in Scheme 1, exemplified by the reaction between (**1b**) and (**2b**). The unoccupied d orbital on the cobalt atom accepts an electron pair from the carbon atom of the diazo compound. Elimination of N_2 then occurs by nucleophilic attack of S on the methylene carbon. In the case of (**1b**), the S atom attached to the C carrying the ester group is more negatively charged and it attacks the methylene carbon, thus explaining the regioselectivity of the addition.

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