Letter

Alkylidene–Dithiocarbamate coupling—crystal structure of $[Ru\{\kappa^2\text{-}CH(C_6H_4OMe\text{-}4)SC(NC_4H_8)S\}\{\kappa^2\text{-}S_2CNC_4H_8\}(CO)(PPh_3)]$

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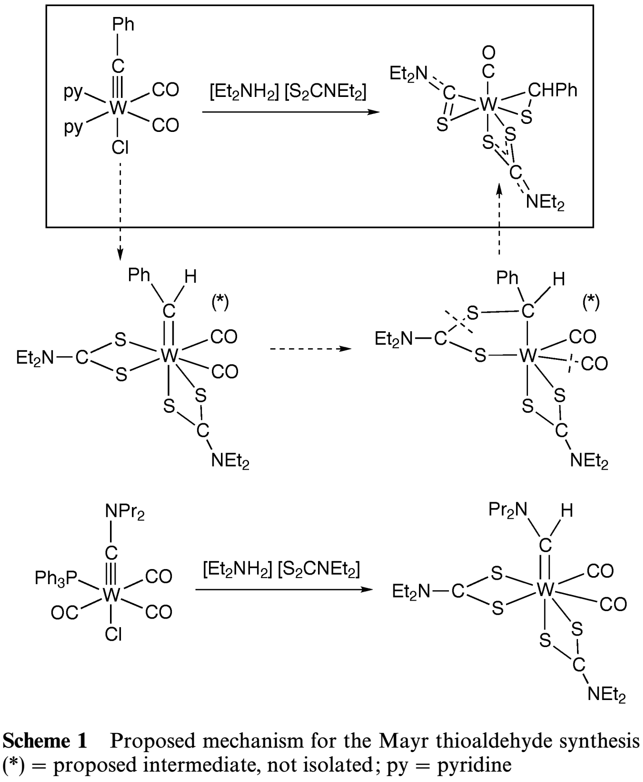
The reaction of $[Ru(\equiv CC_6H_4OMe\text{-}4)Cl(CO)(PPh_3)_2]$ with $[NH_4][S_2CNC_4H_8]$ provides the structurally characterised metallacycle $[Ru\{\kappa^2\text{-}CH(C_6H_4OMe\text{-}4)SC(NC_4H_8)S\}(S_2CNC_4H_8)(CO)(PPh_3)]$, related examples of which arise from the reactions of xanthate or dithiocarbamate salts with the alkylidene compounds $[MCl_2({=}CHR)(CO)(PPh_3)_2]$ (M = Ru or Os; R = Ph or C_6H_4OMe-4) and $[OsCl({=}CHR)(OH_2)(CO)(PPh_3)_2]ClO_4$.

A number of years ago, Mayr *et al.*[1] reported an intriguing conversion of a benzylidyne ligand into coordinated thiobenzaldehyde, upon treatment with dithiocarbamate salts (Scheme 1). In a previous communication, we were able to show for related Group 6 aminomethylidyne complexes that alkylidene complexes were most likely involved in this transformation, formed by initial protonation of the alkylidyne carbon.[2] This supposition leaves the proposed but otherwise unprecedented coupling of alkylidene and dithiocarbamate ligands to be placed on a firm mechanistic footing. Although we have yet to obtain supporting results from the chemistry of Group 6 alkylidenes and alkylidynes, we report herein novel Group 8 metallacycles which result from just such a process. In our pursuit of such a process we have been guided by the results of both Roper and Werner and their co-workers: Roper and co-workers[3] have observed that the methylene complex $[Ru(\eta^2\text{-}OCPh)Cl({=}CH_2)(PPh_3)_2]$ reacts with sodium acetate to provide the metallacyclic acetoxymethyl complex $[Ru(\kappa^2\text{-}CH_2OCMeO)Ph(CO)(PPh_3)_2]$ whilst Werner and co-workers[4] have illustrated the insertion of methyl propiolate into the complex $[Ru(\kappa^2\text{-}O_2CMe)(PPh_3)(\eta\text{-}C_5H_5)]$ to provide the metallacycle $[Ru\{\kappa^2\text{-}C({=}CHCO_2Me)OCMeO\}(PPh_3)(\eta\text{-}C_5H_5)]$.



Scheme 1 Proposed mechanism for the Mayr thioaldehyde synthesis (*) = proposed intermediate, not isolated; py = pyridine

We have recently shown that the benzylidyne complex $[Ru(\equiv CPh)Cl(CO)(PPh_3)_2]$ (**1a**)[5] reacts with carbon disulfide to provide the thioacyl complex $[Ru(\eta^2\text{-}SCPh)Cl(CS)(PPh_3)_2]$[6] and with propylene sulfide to provide $[Ru(\eta^2\text{-}SCPh)Cl(CO)(PPh_3)_2]$.[7] With this clear propensity for C—S bond forming processes we considered $[Ru(\equiv CC_6H_4OMe\text{-}4)Cl(CO)(PPh_3)_2]$ (**1b**) to be a suitable candidate for investigating dithiocarbamate-based C—S bond formation.‡ Somewhat surprisingly, no reaction ensues between (**1b**) and $Na[S_2CNMe_2]\cdot 2H_2O$ at room temperature despite the established lability of the chloride ligand in this complex. Perhaps more surprisingly, a rapid reaction does result on addition of $[NH_4][S_2CNC_4H_8]$ (ammonium pyrollydine dithioate) to provide a yellow coloured solution from which a mixture of two isomers of a compound (**2b**) is obtained. Heating this mixture in chloroform for two days results in clean conversion to the thermodynamic isomer (**2b**)-t. Spectroscopic¶ and crystallographic data (Fig. 1)§ identify (**2b**)-t as the metallacycle $[Ru\{\kappa^2\text{-}CH(C_6H_4OMe\text{-}4)S_2CN(CH_2)_4\}\{\kappa^2\text{-}$

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‡ The anisolyl derivative (**1b**) was chosen for spectroscopic and crystal growing purposes. Similar results were obtained for (**1a**).

§ Crystal data for (**2b**)-t: $C_{37}H_{39}N_2O_2PS_4Ru\cdot CHCl_3$, $M = 923.35$, triclinic, space group $P\bar{1}$ (No. 2), $a = 13.009(1)$, $b = 13.029(2)$, $c = 13.190(1)$ Å, $\alpha = 89.75(1)$, $\beta = 77.19(1)$, $\gamma = 70.44(1)°$, $U = 2048.1(3)$ Å^3, $Z = 2$, $D_c = 1.497$ g cm^{-3}, μ(Mo-Kα) = 8.6 cm^{-1}, $F(000) = 944$. A pale orange prism of dimensions 0.57 × 0.53 × 0.47 mm was used. 7213 Independent reflections were measured on a Siemens P4/PC diffractometer (graphite-monochromated Mo-Kα radiation) using ω scans. The structure was solved by direct methods and all the non-hydrogen atoms were refined anisotropically using full-matrix least squares based on F^2 with absorption-corrected data to give $R_1 = 0.049$, and $wR_2 = 0.112$ for 5514 observed reflections $[|F_o| > 4\sigma(|F_o|), 2\theta \leqslant 50°]$ and 424 parameters.

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$S_2CN(CH_2)_4\}(CO)(PPh_3)]$. Spectroscopic and FAB-MS data¶ for the intermediate (**2b**)-k indicate that it is a kinetically formed isomer of the thermodynamic product (**2b**)-t. It is possible to isolate a pure sample of (**2b**)-k from an alternative synthesis (*vide infra*), and subsequently observe its slow and clean conversion to the thermodynamic product (**2b**)-k [48 h in CH_2Cl_2 at 30 °C] (Scheme 2).

The geometry at ruthenium is pseudo-octahedral, given the constraints of the two chelates, with *cis* angles in the range 84.50(4)–99.45(4)° with the largest angle being between P and S(7) such that the phosphine is displaced in the direction of C(4). The carbonyl is positioned *trans* to the coordinated sulfur of the dithiocarbamatoalkyl, this presumably being the best π-donor of the ligand set. The geometries of the carbonyl, phosphine and dithiocarbamate ligands are as expected for ruthenium(II). The principal feature of interest is the metallacyclic alkyl chelate. The five-membered chelate ring is slightly folded with C(4) lying 0.26 Å out of the least-squares plane defined by Ru, S(1), C(2) and S(3); C and S(7) lie 0.14 and 0.12 Å respectively out of this plane away from the phosphine. The constraints of chelation are satisfied by a closing of the angles at S(3) [106.7(2)] and S(1) [104.8(2)°] and an opening of the Ru—C(4)—S(3) angle [116.0(3)°] whilst those at ruthenium [87.82(13)] and C(2) [122.7(3)°] are close to those expected for the respective hybridisations of these elements. Bond lengths within the metallacycle are generally unremarkable and consistent with the valence bond description indicated in Scheme 2 which invokes a Ru—C(4) single bond [2.163(5) Å], and formal double and single bonds between C(2) and S(1) [1.694(5) Å] and S(3) [1.735(5) Å], respectively. These may be compared internally with values of 1.713(5) and 1.715(5) Å found for C(6)—S(7) and C(6)—S(5), respectively. The dative S(1)—Ru bond [2.431(1) Å] is noticeably shorter than the two ruthenium dithiocarbamate separations [2.470(1), 2.450(1) Å] which is perhaps a reflection of the π-acidity of the *trans* carbonyl ligand.

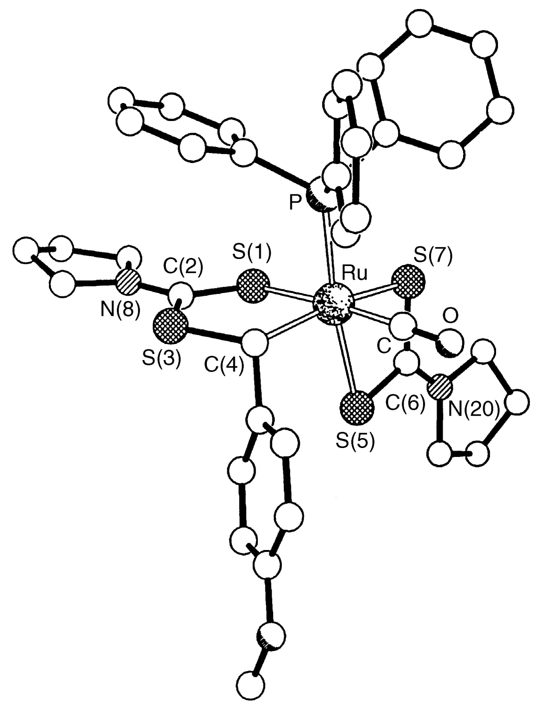
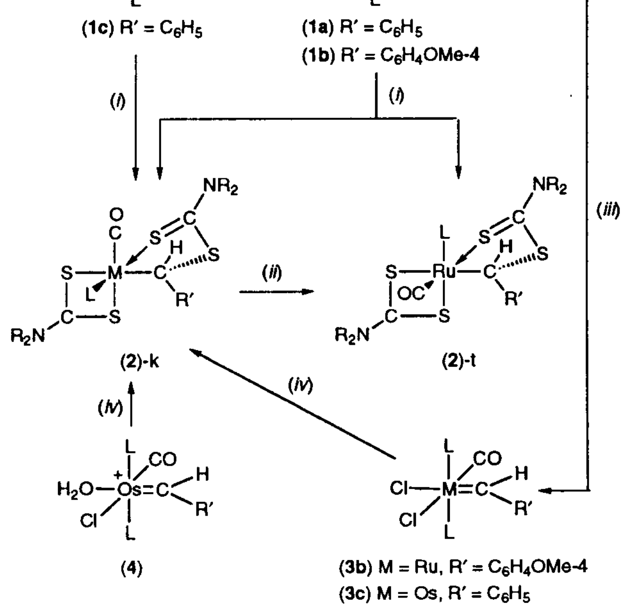


Fig. 1 Molecular geometry of $[Ru\{CH(C_6H_4OMe)SC(NC_4H_8)S\}(S_2CNC_4H_8)(CO)(PPh_3)]$ (**2b**)-t

Turning to the mechanism of formation of (**2b**), it is clear from the failure of (**1b**) to react with $Na[S_2CNMe_2]$,



Scheme 2 *Reagents and conditions*: L = PPh_3; (*i*) $[NH_4][S_2CNC_4H_8]$, 25 °C, CH_2Cl_2, EtOH; (*ii*) CH_2Cl_2, 30 °C, 2 d; (*iii*) NH_4Cl, CH_2Cl_2; (*iv*) $Na[S_2CNMe_2]$ or $NH_4[S_2CNC_4H_8]$, CH_2Cl_2, EtOH

¶ Selected data for new complexes [25 °C, IR (Nujol), NMR ($CDCl_3$), FAB-MS (nba), satisfactory microanalytical data obtained]. $[Ru\{CH(C_6H_4OMe\text{-}4)SC(NC_4H_8)S\}(S_2CNC_4H_8)(CO)(PPh_3]$ (**2b**)-k IR: 1918vs [ν(CO) 1920 (CH_2Cl_2)], 1502m, 1332w, 1243m, 1160s, 997m, 939s, 831 (δC_6H_4) cm^{-1}. NMR: ^1H: δ 1.88 (m, 8 H, CH_2CH_2), 3.37, 3.79 (m × 2, 8 H, NCH_2), 3.65 (s, 3 H, OCH_3), 4.60 [d, 1 H, CHS, *J*(PH) = 40 Hz], 6.43 (s, 4 H, C_6H_4), 7.10–7.66 (15 H, C_6H_5). $^{13}C\{^1H\}$: δ 206.6 (CS_2), 206.0 [d, CO *J*(PC) = 18.3], 205.9 (CS_2), 156.2–112.7 (C_6H_5 and C_6H_4), 55.8, 55.4, 53.5, 48.6, 48.3 (OCH_3 and NCH_2), 46.2 [d, CHS, *J*(PC) = 5.4 Hz], 26.7 (1C), 26.2 (2C), 25.5 (1C) (C_2H_4). ^{31}P $\{^1H\}$: δ 46.6. FAB-MS *m/z* (%) = 804 (8) $[M]^+$, 776 (15) $[M - CO]^+$, 690 (7) $[M - SCN(CH_2)_4]^+$, 658 (42) $[M - S_2CN(CH_2)_4]^+$, 624 (64) $[Ru(PPh_3)_2]^+$, 512 (61) $[M - PPh_3]^+$, 362 (68) $[RuPPh_3]^+$. (**2b**)-t IR: 1914vs [ν(CO) 1920 (CH_2Cl_2)], 1600w, 1502w, 1332m, 1297w, 1243s, 1166s, 948m, 831 (δC_6H_4) cm^{-1}. NMR: ^1H: δ 1.4–2.10 (m, 8 H, C_2H_4), 3.01–3.69 (m, 8 H, NCH_2), 3.67 (s, 3 H, OCH_3), 4.62 [d, 1 H, CHS, *J*(PH) = 5.7], 6.67, 6.94 [$(AB)_2$, 4 H, *J*(AB) = 8.4 Hz], 7.24–7.91 (15 H, C_6H_5). $^{13}C\{^1H\}$: δ 208.0, 204.9 (CS_2), 202.2 [d, CO, *J*(PC) = 15.1] 155.4–113.1 (C_6H_5 and C_6H_4), 55.2, 55.0, 53.3, 49.6, 48.9 (OCH_3 and NCH_2), 39.4 [d, CHS, *J*(PC) = 6.5 Hz], 26.8, 25.4, 24.9 (C_2H_4). ^{31}P $\{^1H\}$: δ 56.5. FAB-MS *m/z* (%) = 804 (6) $[M]^+$, 776 (7) $[M - SCN(CH_2)_4]^+$, 690 (8) $[M - SCN(CH_2)_4]^+$, 658 (17) $[M - S_2CN(CH_2)_4]^+$, 630 (9) $[M - S_2CN(CH_2)_4 - CO]^+$, 624 (17) $[Ru(PPh_3)_2]^+$, 512 (9) $[M - 2(CH_2)_4NCS_2]^+$, 362 (24) $[RuPPh_3]^+$. $[Os\{CHPhSC(NMe_2)S\}(S_2CNMe_2)(CO)(PPh_3)]$ (**2c**)-k IR: 1895vs [ν(CO), 1901 (CH_2Cl_2)] 1504m, 1257m, 1149m, 981w, 964w cm^{-1}. NMR: ^1H: δ 3.10, 3.11, 3.12, 3.18 (s × 4, 3 H × 4, NCH_3), 5.46 [br d, 1 H, *J*(PH) = 2.6 Hz], 6.89–7.89 (20 H, C_6H_5). $^{13}C\{^1H\}$: δ 214.9, 212.9 (CS_2), 182.7 [d, CO, *J*(PC) = 10.2], 155.1–123.3 (C_6H_5), 47.4, 44.0, 39.2, 38.1 (NCH_3), 23.1 [d, CHS, *J*(PC) = 5.4 Hz]. ^{31}P $\{^1H\}$: δ 13.9. FAB-MS *m/z* (%) = 812 (88) $[M]^+$, 784 (22) $[M - CO]^+$, 722 (13) $[M - CHPh]^+$, 690 (68) $[M - S_2CNMe_2]^+$, 662 (38) $[M - CO - S_2CNMe_2]^+$, 572 (11) $[OsPPh_3S_2CNMe_2]^+$. N.b. After stirring for 5 d at 40 °C, 40% conversion to the thermodynamic isomer could be spectroscopically observed: NMR: ^1H: δ 2.44, 2.79, 3.50, 3.64 (s × 4, 3 H × 4, NCH_3), 6.16 [d, 1 H, OsCHS, *J*(PH) = 7.3 Hz]. ^{31}P $\{^1H\}$: δ 14.7. $[Ru\{CH(C_6H_4OMe\text{-}4)SC(OEt)S\}(S_2COEt)(CO)(PPh_3)]$ (**5**) IR: 1945vs [ν(CO), 1957 (CH_2Cl_2)] cm^{-1}. NMR: ^1H: δ 1.31, 1.39 (t × 2, 3 H × 2, CH_3), 3.46, 4.51 (q × 2, 2 H × 2, OCH_2), 6.13 (br d, 1 H, RuCHS), 6.70, 6.91 [$(AB)_2$, 4 H, C_6H_4, *J*(AB) = 8, 7 Hz], 7.23–7.93 (m, 15 H, C_6H_5). $^{13}C\{^1H\}$: δ 231.7, 229.9 (CS_2), 200.5 [d, CO, *J*(PC) = 15.3], 156.0–113.4 (C_6H_4 and C_6H_5), 72.0, 67.5, 66.0 (OCH_2 and OCH_3), 35.2 [br d, CHS, *J*(PC) not resolved], 14.1 (CH_3). ^{31}P $\{^1H\}$: δ 56.8. FAB-MS *m/z* (%) = 754 (7) $[M]^+$, 726 (63) $[M - CO]^+$, 633 (21) $[M - S_2COEt]^+$, 605 (22) $[M - S_2COEt - CO]^+$, 485 (64) $[M - 2S_2COEt - CO]^+$.

that the complexes $[Ru(\equiv CC_6H_4OMe\text{-}4)\{\kappa^a\text{-}S_2CN(CH_2)_4\}(CO)(PPh_3)_b]$ ($a + b = 3$) are unlikely intermediates. The ammonium cation in $[NH_4][S_2CN(CH_2)_4]$ therefore appears to be acting as a proton donor to convert (**1b**) into a cationic alkylidene species. In support of this we note that (**1b**) reacts cleanly with NH_4Cl to provide $[RuCl_2(=CHC_6H_4OMe\text{-}4)(CO)(PPh_3)_2]$ (**3b**).[8] Both (**3b**) and the complexes $[OsCl_2(=CHPh)(CO)(PPh_3)_2]$ (**3c**)[5] and $[OsCl(=CHPh)(OH_2)(CO)(PPh_3)_2]ClO_4$ (**4**)[5] react with $Na[S_2CNMe_2]$ to provide analogous metallacyclic complexes¶ with the following points to note. (*i*) With the alkylidene having been preformed, sodium salts suffice. (*ii*) In the case of osmium, the kinetic isomer (**2c**)-k is isolated and consistent with slower rates of isomerism for heavier elements, does not undergo isomerism at room temperature. In a similar manner the complex $[Ru\{CH(C_6H_4OMe\text{-}4)SC(OEt)S\}(S_2COEt)(CO)(PPh_3)]$ (**5**)¶ results from the reaction of (**3b**) with potassium ethyl xanthate.

The processes illustrated herein give an indication as to how the Mayr thioaldehyde synthesis might proceed. The final step, the scission of the metallacycle, does not proceed in the case of (**2b**) to provide the as yet hypothetical thioaldehyde complex $[Ru(SCHC_6H_4OMe\text{-}4)(\eta^2\text{-}SCNC_4H_8)(S_2CNC_4H_8)L]$ ($L = CO$ or PPh_3) although thioaldehyde complexes of ruthenium and osmium have precedent.[9] Nevertheless such metallacyclic species are clearly plausible in the formation of $[W(\eta^2\text{-}SCHPh)(CO)(\eta^2\text{-}SCNEt_2)(\kappa^2\text{-}S_2CNEt_2)]$.

Dithiocarbamates are typically considered to act as spectator co-ligands, seldom taking a direct part in ligand transformation processes. The results described above compliment Hogarth *et al.*'s[10] discovery of multiple nitrene insertions into the Cu—S bonds of dithiocarbamate complexes. Taken together it appears that the superficial innocence of these ligands masks a potentially rich underlying chemistry. Accordingly we are now investigating the interactions of dithiocarbamates with a wide range of metal—carbon multiple bonds.

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