Thio- and Seleno-acrylamide Derivatives from Ynamines and Transition Metal-co-ordinated Thio- and Seleno-aldehydes and -ketones

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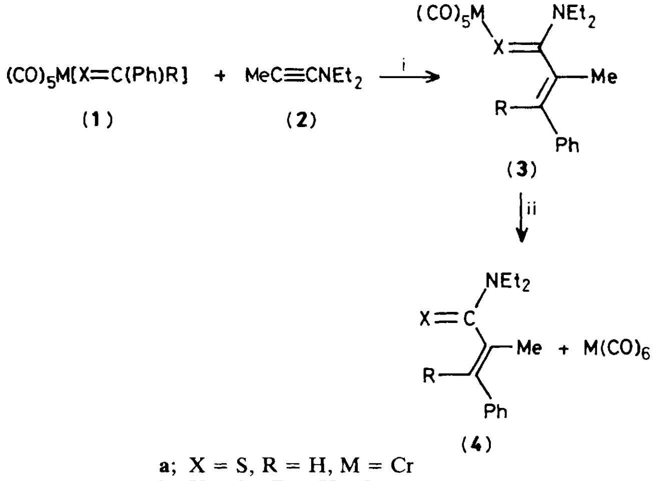
Pentacarbonyl-chromium- and -tungsten-co-ordinated thio- and seleno-aldehydes and selenoketones, respectively, react with 1-diethylaminoprop-1-yne *via* regiospecific [2 + 2] cycloaddition and stereospecific electrocyclic ring-opening to give metal-co-ordinated thio- and seleno-acrylamide derivatives which can be cleaved almost quantitatively from the metal by CO (100 atm).

Monomeric selenobenzaldehydes and diarylselenoketones are not stable as free species,[1] although they can be generated and trapped *in situ* as cycloadducts with conjugated dienes.[2] In contrast, transition metal complexes of selenoaldehydes and selenoketones are stable.[3,4] However, when bonded to a pentacarbonyl-chromium or -tungsten fragment the extremely high reactivity of the free seleno-aldehydes and -ketones is reduced. This has already been demonstrated by their facile reaction with 1,3-dienes to give metal-co-ordinated selenacycles.[5] We now report that transition metal-co-ordinated thioaldehydes, selenoaldehydes, and selenoketones can also be employed as easily accessible synthetic building blocks for the synthesis of selenoacrylamide derivatives.

When deep blue solutions of the thioaldehyde,[6] selenoaldehyde,[4] and selenoketone complexes[7] (**1a**—**d**), respectively, were treated in dichloromethane at −30 °C (**1a,b**) or at ambient temperature (**1c,d**) with a slight excess of 1-diethylaminoprop-1-yne (**2**), the solution immediately turned orange and the thio- and seleno-acrylamide derivatives (**3a**—**d**) were formed almost quantitatively (Scheme 1). Purification of (**3a**—**d**) by column chromatography followed by recrystallization from pentane–dichloromethane gave compounds (**3a**—**d**) in 72—95% yield. The complexes were characterized by



a; X = S, R = H, M = Cr
b; X = Se, R = H, M = W
c; X = Se, R = Ph, M = Cr
d; X = Se, R = Ph, M = W

Scheme 1. i, (**1**) : (**2**) *ca.* 1 : 1.2, dichloromethane; ii, Et_2O, CO (100 atm), 70 °C, 10—15 h.

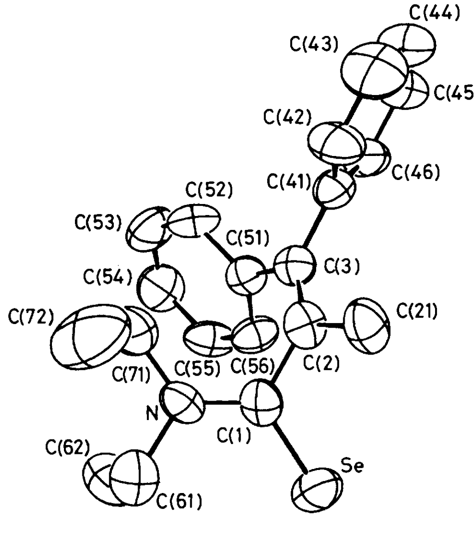


Figure 1. Molecular structure of (**4c**) (ORTEP, thermal ellipsoids 50%, without hydrogen atoms). Important distances (Å) and angles (°) are: C(1)–Se 1.837(4), C(1)–N 1.329(7), N–C(61) 1.494(8), N–C(71) 1.492(7), C(1)–C(2) 1.496(7), C(2)–C(3) 1.345(7); Se–C(1)–N 122.9(4), Se–C(1)–C(2) 118.8(4), N–C(1)–C(2) 118.3(4), C(1)–N–C(61) 121.1(4), C(1)–N–C(71) 124.7(5), C(61)–N–C(71) 114.3(5).

elemental analysis and by spectroscopic means.† The 'insertion' of the C≡C bond into the X=C bond is regiospecific. According to the ^{1}H n.m.r. spectra of (**3a,b**), the reaction is also stereospecific. Only one isomer for R = H was obtained; the formation of more than 2% of the other isomer would have been detected. Based on a comparison with published data for related thioamides,[8] we tentatively assign the (*E*) configuration (Me and Ph being *cis*) to the isomer formed. The ν(CO) vibrations in the i.r. spectra† of (**3a**—**d**) indicate that the X=C(NEt$_2$)C(Me)=C(Ph)R ligand is σ-bonded. The corresponding η^2-isomer should absorb at higher wavenumber (*ca.* 20—40 cm^{-1}).[4]

The uncomplexed thio- and seleno-acrylamides (**4a**—**c**) were obtained almost quantitatively when CO (100 atm; 50 °C; 10—15 h) was applied to solutions of complexes (**3a**—**d**) in diethyl ether. Additionally, M(CO)$_6$ (M = Cr, W) was formed (Scheme 1) which is the starting material for the synthesis of (**1**). On cleavage of the M–X bond, the stereochemistry of the organic molecule was preserved. The thio- and seleno-acrylamides were characterized spectroscopically,‡ by elemental analyses and, in the case of (**4c**), by an *X*-ray structure determination (Figure 1).§

The Se–C bond length [1.837(4) Å] is halfway between the Se–C single bond value of 1.98(1) Å in dimethyl selenide[9] and 1.692(2) Å for the cumulated double bond in CSe$_2$.[10] The C(1)–N bond length [1.329(7) Å] indicates substantial multiple bond character which is in line with the almost ideal planarity of the amino-substituted selenocarbonyl group [*i.e.* atoms C(2), C(1), Se, N, C(61), C(71)]. This plane forms an angle of 66.5° with that of the alkenic double bond.

The formation of the complexes (**3a**—**d**) can be rationalized as proceeding *via* regiospecific [2 + 2] cycloaddition of the C≡C bond of the alkyne to the metal-co-ordinated X=C bond with subsequent stereospecific electrocyclic ring-opening. Kinetic investigations of the reaction of (**2**) with the selenoketone complexes (**1c**) and (**1d**) indicate that the addition step is rate-determining. Since the influence of the solvent on the reaction rate is only very small, a dipolar transition state can be excluded. The results show that complexes of the type (**1**) can be employed as useful sources of the X=C fragment (X = S, Se) in organic synthesis.

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support of this work.

Received, 21st November 1986; Com. 1659

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† *Selected spectroscopic data.* (**3a**): I.r. ν_{CO} (hexane) 2063 w, 1979 vw, 1939 vs, 1916 s cm^{-1}; ^{1}H n.m.r. δ (CD$_3$COCD$_3$) 1.29 (t, *J* 6.8 Hz, Et), 1.32 (t, *J* 6.4 Hz, Et), 2.19 (s, Me), 6.52 (s, =CH); ^{13}C n.m.r. δ (CD$_3$COCD$_3$) 203.5 (C=S).

(**3b**): I.r. ν_{CO} (hexane) 2066 w, 1972 vw, 1934 vs, 1913 m cm^{-1}; ^{1}H n.m.r. δ (CD$_3$COCD$_3$) 1.34 (t, *J* 7.1 Hz, Et), 1.42 (t, *J* 7.1 Hz, Et), 2.18 (s, Me), 6.50 (s, =CH); ^{13}C n.m.r. δ (CD$_3$COCD$_3$) 204.5 (C=Se).

(**3c**): I.r. ν_{CO} (hexane) 2060 w, 1936 s, 1916 m cm^{-1}; ^{1}H n.m.r. δ (CD$_3$COCD$_3$) 0.93 (t, *J* 7.1 Hz, Et), 1.15 (t, *J* 7.1 Hz, Et), 2.21 (s, Me); ^{13}C n.m.r. δ (CD$_3$COCD$_3$) 205.7 (C=Se).

(**3d**): I.r. ν_{CO} (hexane) 2068 w, 1971 vw, 1934 vs, 1913 m cm^{-1}; ^{1}H n.m.r. δ (CD$_3$COCD$_3$) 0.95 (t, *J* 7.1 Hz, Et), 1.16 (t, *J* 7.1 Hz, Et), 2.26 (s, Me); ^{13}C n.m.r. δ (CD$_3$COCD$_3$) 203.5 (C=Se).

‡ *Selected spectroscopic data.* (**4a**): ^{1}H N.m.r. δ (CD$_3$COCD$_3$) 1.26 (t, *J* 7.1 Hz, Et), 1.29 (t, *J* 7.1 Hz, Et), 2.14 (d, *J* 1.5 Hz, Me), 3.71 (q, *J* 7.1 Hz, C*H*$_2$), 4.02 (q, *J*, 7.1 Hz, C*H*$_2$), 6.28 (q, *J* 1.5 Hz, =CH); ^{13}C n.m.r. δ (CD$_3$COCD$_3$) 203.6 (C=S); (**4c**): ^{1}H n.m.r. δ (CD$_3$COCD$_3$) 0.88 (t, *J* 7.1 Hz, Et), 1.12 (t, *J* 7.1 Hz, Et), 2.12 (s, Me); ^{13}C n.m.r. δ (CD$_3$COCD$_3$) 205.7 (C=Se).

§ *Crystal data* for (**4c**): $C_{20}H_{23}NSe$, M = 356.4, orthorhombic, space group $P2_12_12_1$, a = 9.245(1), b = 11.820(1), c = 16.726(1) Å, U = 1827.8 Å^3, D_c = 1.295 g cm^{-3}, Z = 4 (22 °C), μ(Mo-K_α) = 20.3 cm^{-1}. 3195 unique reflections were recorded, of which 2167 were 'observed' with $I \geqslant 2.0\,\sigma(I)$ (θ–2θ scan) using Mo-K_α radiation (λ 0.71069 Å, graphite monochromator) on an Enraf–Nonius CAD-4 diffractometer. Lorentz–polarisation and empirical absorption correction, solution by automated Patterson methods (SHELXS-86), R (R_w) = 0.040 (0.027), $w = 1/\sigma^2(F_o)$ for 200 refined parameters (anisotropic, H atoms fixed, GFMLX). 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.