

Investigation of the dithiocarbamate-induced coupling of allylidene and carbonyl ligands on a tungsten center

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Abstract

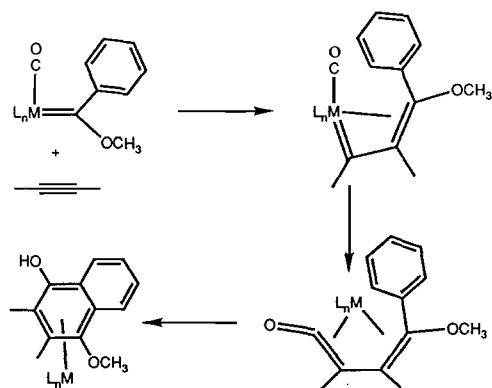
Reaction of the allylidene tungsten complex $[\text{W}(\text{CPhCHCHMe})\text{Br}_2(\text{CO})_2(4\text{-picoline})]$ (**1**) with the dithiocarbamates MS_2CNR_2 (a: M=Na, R=Et; b: M=Na, R=Me; c: M=Li, R=Ph) in THF at 50 °C affords the vinylketene tungsten complexes $[\text{W}(\text{S}_2\text{CNR}_2)_2(\text{OCCPhCHCHMe})(\text{CO})]$ (**2a–c**). At lower temperatures, four reaction intermediates (**3–6**) may be discerned. Spectroscopic studies indicate that these compounds contain η^4 -allyldithiocarbamate ligands which are generated by addition of dithiocarbamate across the metal–carbon double bond of the allylidene–tungsten unit in **1**. The structures of $[\text{W}(\text{S}_2\text{CNET}_2)_2(\text{OCCPhCHCHMe})(\text{CO})]$ (**2a**) and of one intermediate, $[\text{W}(\eta^4\text{-Et}_2\text{NCS}_2\text{CPhCHCHMe})(\text{S}_2\text{CNET}_2)(\text{CO})_2]$ (**5a**) were elucidated by X-ray crystallography.

Key words: Coupling reaction; Dithiocarbamate ligand; Tungsten complexes; Carbonyl complexes; Allylidene complexes

Introduction

The carbonylation of allylidene, or vinylcarbene, ligands to form vinylketene ligands has been implicated as a key step in the Dötz reaction and in related organometallic transformations [1, 2]. Recently, we described the structure and dynamic behavior of several allylidene tungsten complexes [3]. Based on theoretical

studies by Hofmann *et al.* [4], these compounds are similar in their electronic properties to the allylidene chromium complexes which were postulated as intermediates in the Dötz reaction. The observation [5] of allylidene–carbonyl coupling in these tungsten systems is therefore of significance. This paper gives a full account of our study of the dithiocarbamate-induced coupling of allylidene and carbonyl ligands. Several other examples of allylidene–carbonyl coupling in well-defined systems have been described in the literature [6].



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Experimental

Standard inert-atmosphere techniques were used in the execution of the experiments. The solvents methylene chloride (CaH_2), tetrahydrofuran (Na/benzophenone) and hexane (CaH_2) were dried and distilled prior to use. Complex **1** was prepared as previously reported [3]. $\text{NaS}_2\text{CNET}_2$ and $\text{NaS}_2\text{CNMe}_2$ were obtained from commercial sources and dried under vacuum for 6 h at 110 °C. $\text{LiS}_2\text{CNPh}_2$ was prepared by the reaction of LiNPh_2 with CS_2 in THF and recrystallization from ether [7]. The NMR spectra were measured at 250 or 300 MHz (for ^1H NMR) in CDCl_3 at room temperature unless otherwise noted; solvent peaks were

used as internal reference, the chemical shifts are reported in δ relative to TMS.

[W(S₂CNEt₂)₂(η^4 -OCPhCHCHCH₃)(CO)] (2a)

A slurry of **1** (0.168 g, 0.270 mmol) in THF (15 ml) was stirred at ambient temperature as a solution of NaS₂CNEt₂ (0.094 g, 0.55 mmol) in THF (0.5 ml) was added dropwise. The initially deep brown slurry immediately changed to a cloudy, deep orange-red solution. The mixture was then heated to 50 °C for 2 h. When the reaction was judged complete by IR spectroscopy, the solvent was removed under reduced pressure. The residue was extracted with methylene chloride (c. 10 ml) in several small portions, and the extracts were filtered through Celite on a fritted disk. Cooling of a saturated solution of the product in methylene chloride/hexane from 50 to -78 °C gave a mixture of shiny red needles and prisms of **2a**·CH₂Cl₂ (0.184 g, 0.244 mmol, 90.4%). IR (CH₂Cl₂, cm⁻¹): ν (CO) = 1936 (s), 1720 (m, br). ¹H NMR (CDCl₃) (major isomer, 87%): δ 7.39–7.43 (m, 2H, C₆H₅), 7.17–7.25 (m, 2H, C₆H₅), 7.07–7.12 (m, 1H, C₆H₅), 5.30 (d, J = 7.82 Hz, 1H, CH), 5.28 (s, 2H, CH₂Cl₂), 3.26–3.80 (m, 8H, NCH₂ and CHMe), 2.80–2.94 (m, 1H, NCH₂), 2.01 (d, J = 6.34 Hz, 3H, CHCH₃), 1.24 (t, J = 7.24 Hz, 3H, NCH₂CH₃), 1.22 (t, J = 7.14 Hz, 3H, NCH₂CH₃), 1.11 (t, J = 7.21 Hz, 3H, NCH₂CH₃), 0.60 (t, J = 7.15 Hz, 3H, NCH₂CH₃); (minor isomer, 13%, partially visible): δ 7.29–7.35 (m, 2H, C₆H₅), 4.93 (d, J = 7.91 Hz, 1H, CH), 2.32 (d, J = 6.35 Hz, 3H, CHCH₃). ¹³C NMR (CDCl₃) (major isomer): δ 234.9 (d, ³ J_{CH} = 1.2 Hz, C=O), 214.5 (s, CO), 214.1 (s, CS₂), 204.7 (s, CS₂), 128.6 (s, *ipso*-C₆H₅), 128.4 (d, ¹ J_{CH} = 158.6 Hz, C₆H₅), 127.2 (d, ¹ J_{CH} = 164.0 Hz, C₆H₅), 126.6 (d, ¹ J_{CH} = 159.6 Hz, C₆H₅), 79.4 (d, ¹ J_{CH} = 180.15 Hz, CH), 68.9 (d, ¹ J_{CH} = 162.8 Hz, CHMe), 56.1 (s, CPh), 53.4 (t, ¹ J_{CH} = 177.41 Hz, CH₂Cl₂), 45.1 (q, NCH₂), 44.3 (q, NCH₂), 44.1 (t, ¹ J_{CH} = 136.9 Hz, NCH₂), 19.6 (q, ¹ J_{CH} = 127.9 Hz, CH₃), 12.4 (q, ¹ J_{CH} = 128.4 Hz, 2NCH₂CH₃), 12.2 (q, NCH₂CH₃), 11.7 (q, NCH₂CH₃).

Variable temperature NMR study of the reaction between [W(CPhCHCHCH₃)(Br)₂(CO)₂(4-pic)] (1) and NaS₂CNEt₂

¹H NMR sample. A cold (-78 °C) solution of NaS₂CNEt₂ (0.0125 g, 0.0730 mmol) in d₈-THF (0.45 ml) was added to a cold (-78 °C) slurry of **1** (0.023 g, 0.037 mmol) in d₈-THF (0.25 ml). No reaction appeared to occur at -78 °C, and the stirred mixture was slowly warmed to -45 °C over a period of 30 min. The cloudy, brownish orange solution was then quickly transferred to a cold (-78 °C) NMR tube under N₂. The tube was placed into an NMR probe at 228 K, and spectra were recorded after the probe was allowed to equilibrate at each temperature (228–328 K) for

about 20 min. **3a**: (228 K) δ 4.7 (d, J = 8.33 Hz, 1H, CH), 2.4 (br, s, 3H, CH₃-pic), 2.1 (br d, J = 6.2 Hz, 3H, CH₃). **4a**: (228 K) δ 4.8 (d, J = 8.6 Hz, 1H, CH); 2.2 (br s, 3H, CH₃-pic). The singlets at δ 2.4 and 2.2 ppm for **3a** and **4a**, respectively, indicate that compounds **3a** and **4a** each still contain bound 4-picoline. **5a**: (228 K) δ 5.3 (d, J = 5.6 Hz, 1H, CH), 3.28 (m, 1H, CHMe), 2.3 (d, J = 6.0 Hz, 3H, CH₃). **6a**: (298 K) δ 3.45 (d, J = 9.00 Hz, 1H, CH), 2.56 (m, 1H, CHMe), 2.06 (d, J = 5.87 Hz, CH₃).

¹³C NMR sample. A solution of NaS₂CNEt₂ (0.053 g, 0.32 mmol) in d₈-THF (0.5 ml) was added to a cold (-78 °C) slurry of **1** (0.097 g, 0.16 mmol) in d₈-THF (1 ml). The stirred mixture was slowly warmed to -35 °C, cooled to -78 °C, and quickly transferred to an NMR tube (-78 °C), using an additional 0.5 ml d₈-THF to rinse the reaction flask. The tube was placed into an NMR probe at 228 K. The ¹H NMR spectrum of the sample indicated that the organometallic material was 66% **5a** and 34% **3a** and **4a**. **3a** and **4a**: (238 K) δ 229.7, 227.6, 221.0, 220.1, 205.9, 201.3, 76.1, 74.5, 65.3, 64.2, 62.7, 49.1, 46.5, 44.8, 44.2, 20.7, 19.7, 16.8, several peaks clustered at 11–13. **5a**: (238 K) δ 231.5 (s, J_{WC} = 157.0 Hz), 224.6 (s, J_{WC} = 159.0 Hz), 211.4 (s), 205.0 (s), 150.4 (dd, ¹ J_{CH} = 165.6 Hz, ² J_{CH} = 10.7 Hz), 147.5 (s), 145.0 (s), 128.3 (d, ¹ J_{CH} = 153.4 Hz), 126.4 (d, ¹ J_{CH} = 158.3 Hz), 125.6 (d, ¹ J_{CH} = 158.0 Hz), 125.2 (d, ¹ J_{CH} = 157.5 Hz), 73.8 (s), 71.4 (d, ¹ J_{CH} = 176.7 Hz), 56.2 (d, ¹ J_{CH} = 162.4 Hz), 53.7 (t, ¹ J_{CH} = 140.0 Hz), 50.0 (t, ¹ J_{CH} = 140.0 Hz), 45.0 (d, ¹ J_{CH} = 140.0 Hz), 43.6 (t, ¹ J_{CH} = 140.0 Hz), 21.7 (q, ¹ J_{CH} = 127.5 Hz), 20.9 (q, ¹ J_{CH} = 127.5 Hz), 12.0–12.7 (4 q, ¹ J_{CH} = 127 Hz).

*Reaction of [W(*CPhCHCHCH₃)(Br)₂(*CO)₂(4-pic)] (1') with NaS₂CNEt₂*

A solution of NaS₂CNEt₂ (0.101 g, 0.587 mmol, 2.0 equiv.) in d₈-THF (2 × 0.5 ml) was added to a cold (-78 °C) slurry of [W(*CPhCHCHCH₃)(Br)₂(*CO)₂(4-pic)] (c. 50% ¹³C-enriched in the positions marked by asterisks, 0.181 g, 0.290 mmol) in d₈-THF (1 ml). The sample was warmed to 0 °C for 12 min, then quickly cooled to -35 °C. The ¹H NMR spectrum indicated that the organometallic material was 95% **5a'** and 5% **6a'**. ¹³C{¹H} NMR (238 K) **5a'**: δ 231.5 (s, J_{WC} = 157.1 Hz, CO), 224.6 (s, J_{WC} = 158.8 Hz, CO), 144.9 (d, ¹ J_{CC} = 54.5 Hz, *ipso*-C₆H₅), 73.8 (s, J_{WC} = 16.1 Hz, CPh), 71.3 (d, ¹ J_{CC} = 42.4 Hz, CH), 56.2 (d, ² J_{CC} = 6.7 Hz, CHMe), 53.7 (s), 50.0 (s), 45.0 (s), 43.6 (s) (NCH₂), 21.7 (s, CH₃), 20.9 (s, CH₃-pic), 12.7 (s), 12.6 (s), 12.3 (s), 12.0 (s) (NCH₂CH₃).

The temperature was then raised from -35 to +10 °C for 30 min, then lowered to 0 °C. The ¹H NMR spectrum indicated that the mixture was c. 70% **6a'** and 30% **5a'**, with a trace of **2a'** visible. ¹³C{¹H} NMR (273 K) **6a'**: δ 223.7 (m, J_{WC} = 157.5 Hz, CO), 221.4

(d, $^2J_{CC}=7.5$ Hz, $J_{WC}=144.5$ Hz, CO), 142.3 (d, $^1J_{CC}=56.7$ Hz, *ipso*-C₆H₅), 70.4 (d, $^1J_{CC}=43.1$ Hz, CH), 63.7 (m, CPh), 56.8 (s, CHMe), 51.8 (s), 49.1 (s), 45.4 (s), 44.4 (s) (NCH₂), 20.9 (s, CH₃-pic), 18.8 (d, $^3J_{CC}=5.6$ Hz, CH₃), 11.9–12.8 (NCH₂CH₃).

The temperature was then raised from 0 to +50 °C for 50 min, then lowered to +20 °C. The ¹H NMR spectrum showed the presence of a 95:5 mixture of the isomers of **2a'**. ¹³C{¹H} NMR (293 K) **2a'** (major isomer): δ 231.3 (m, $^1J_{CC}=47.1$ Hz, $^2J_{CC}=7.1$ Hz, C=O), 215.6 (d, $^2J_{CC}=7.1$ Hz, $J_{WC}=155.4$ Hz, CO), 79.9 (d, $^1J_{CC}=46.0$ Hz, CH), (the peak for CHMe is probably obscured by the resonances of d₈-THF), 54.9 (d, $^1J_{CC}=47.0$ Hz, CPh), 45.7 (s), 45.0 (s), 44.9 (s), 44.7 (s), 44.5 (s) (NCH₂), 21.0 (s, CH₃-pic), 19.8 (CH₃), 12.7, 12.5, 12.2 (NCH₂CH₃); **2a'** (minor isomer): δ 237.8 (d, $^1J_{CC}=44.3$ Hz, $^2J_{CC}=5.2$ Hz, C=O), 216.3 (d, $^2J_{CC}=5.1$ Hz, CO), 57.0 (d, $^1J_{CC}=44.4$ Hz, CPh).

$[W(S_2CNMe_2)_2(\eta^4\text{-OCCPhCHCHCH}_3)(CO)]$ (**2b**)

This compound was prepared by a procedure analogous to that described for **2a**. A solution of NaS₂CNMe₂ (0.085 g, 0.59 mmol) in tetrahydrofuran (1 ml) was added to a stirred slurry of **1** (0.175 g, 0.28 mmol) in THF (20 ml), which was initially kept at 0 °C. The reaction was driven to completion by heating to 45–50 °C for 1.5 h. The product was recrystallized by slow cooling of a saturated methylene chloride/hexane solution from ambient temperature to –78 °C to give an orange powder (0.181 g, 0.30 mmol, 96.5%). IR (CH₂Cl₂, cm⁻¹): ν(CO)=1932 (s), 1726 (m, br). ¹H NMR (CDCl₃) (major isomer, 87%): δ 7.39–7.44 (m, 2H, C₆H₅), 7.23–7.29 (m, 2H, C₆H₅), 7.06–7.13 (m, 1H, C₆H₅), 5.38 (d, $J=7.82$ Hz, 1H, CH), 3.40–3.46 (m, 1H, CHMe), 3.23 (s, 3H, NCH₃), 3.21 (s, 3H, NCH₃), 2.92 (s, 3H, NCH₃), 2.50 (s, 3H, NCH₃), 2.00 (d, $J=6.37$ Hz, 3H, CH₃); (minor isomer, 13%, partially visible): δ 4.91 (d, $J=7.67$ Hz, 1H, CH), 3.27 (s, 3H), 3.21 (s, 3H), 3.19 (s, 3H), 3.07 (s, 3H), 2.32 (d, $J=6.33$ Hz, 3H, CH₃). ¹³C NMR (CD₂Cl₂) (major isomer): δ 233.4 (d, $^3J_{CH}=10.4$ Hz, C=O), 215.5 (s, CS₂), 215.2 (s, CO), 206.4 (s, CS₂), 129.1 (d, $J_{CH}=161.2$ Hz, C₆H₅), 128.7 (s, *ipso*-C₆H₅), 127.4 (d, $J_{CH}=164.7$ Hz, C₆H₅), 127.1 (d, $J_{CH}=159.2$ Hz, C₆H₅), 81.0 (d, $J_{CH}=167.8$ Hz, CH), 70.8 (d, $J_{CH}=165.1$ Hz, CHMe), 55.4 (s, CPh), 39.8, 39.5, 38.9, 30.1 (all q, $J_{CH}=140$ Hz, NCH₃), 19.9 (q, $J_{CH}=127.7$ Hz, CH₃).

Variable temperature NMR study of the reaction between $[W(CPhCHCHCH_3)(Br)_2(CO)_2(4\text{-pic})]$ (**1**) and NaS₂CNMe₂

¹H NMR sample. A solution of NaS₂CNMe₂ (0.008 g, 0.054 mmol) in d₈-THF (0.20 ml) was added to a cold (–78 °C) slurry of **1** (0.016 g, 0.026 mmol) in d₈-THF (0.50 ml). No reaction appeared to occur at –78

°C, and the stirred mixture was slowly warmed to –35 °C. The cloudy, red–orange solution was cooled to –78 °C and quickly transferred under N₂ to an NMR tube which was precooled to –78 °C. The tube was placed into an NMR probe at 238 K. ¹H NMR spectra were recorded at this and increasing temperatures after allowing the probe to equilibrate at each temperature (238–331 K) for about 20 min. **3b**: (238 K) δ 4.68 (d, $J=7.95$ Hz, 1H, CH), 2.18 (br s, 3H, CH₃-pic), 2.10 (br d, $J=6.99$ Hz, 3H, CH₃). **4b**: (238 K) δ 4.76 (d, $J=8.74$ Hz, 1H, CH), 2.38 (br s, 3H, CH₃-pic), 1.18 (d, $J=6.34$ Hz, 3H, CH₃). **5b**: (268 K) δ 5.27 (d, $J=5.69$ Hz, 1H), 3.48 (s, 3H, NCH₃), 3.46 (s, 3H, NCH₃), 3.29 (m, 1H, CHMe), 3.19 (s, 3H, NCH₃), 2.96 (s, 3H, NCH₃), 2.28 (d, $J=6.03$ Hz, 3H, CH₃). **6b**: (301 K) δ 3.46 (d, $J=8.92$, 1H, CH), 3.43 (s, 3H, NCH₃), 3.37 (s, 3H, NCH₃), 3.16 (s, 3H, NCH₃), 3.12 (s, 3H, NCH₃), 2.54 (m, CHMe), 2.06 (d, $J=5.58$ Hz, CH₃).

$[W(S_2CNPh_2)_2(\eta^4\text{-OCCPhCHCHCH}_3)(CO)]$ (**2c**)

This compound was prepared by a procedure analogous to that described for **2a**. A solution of LiS₂CNPh₂·0.60 Et₂O (0.199 g, 0.665 mmol) in tetrahydrofuran (4 ml) was added at 0 °C to a stirred slurry of **1** (0.204 g, 0.328 mmol) in tetrahydrofuran (22 ml). The reaction was driven to completion by heating to 50 °C for 1 h. Complex **2c** proved to be considerably less stable than the diethyldithiocarbamate analogue and partially decomposed during this time. The product was purified by column chromatography on silica gel with methylene chloride as the eluant. The initial, brown fractions showed no carbonyl bands in their IR spectra. The orange–red fraction was reduced to an oily residue, which was crystallized by slow cooling of a saturated methylene chloride/hexane solution from ambient temperature to –10 °C to give a red–orange solid (0.111 g, 0.130 mmol, 39.5%). IR (CH₂Cl₂, cm⁻¹): ν(CO)=1935 (s), 1734 (m, br). ¹H NMR (d₈-THF, 195 K) (major isomer, 95%): δ 7.13–7.55 (m, 25H, NPh₂ and C₆H₅), 5.42 (d, $J=7.69$ Hz, 1H, CH), 3.06–3.17 (m, 1H, CHMe); 1.88 (d, $J=6.34$ Hz, 3H, CH₃); (minor isomer, 5%, partially visible): δ=5.10 (d, $J=7.68$ Hz, 1H, CH), 2.77–2.90 (m, 1H, CHMe), 2.18 (d, $J=6.27$ Hz, 3H, CH₃). ¹³C{¹H} NMR (d₈-THF) (major isomer): δ 230.2 (C=O), 221.2, 215.4, 211.1 (2 CS₂ and CO), 142.2–142.8 (Ph), 127.6–130.0 (Ph), 78.8 (CH), 54.9 (CPh), 19.8 (CH₃), resonance of CHMe obscured by solvent.

Variable temperature NMR study of the reaction between $[W(CPhCHCHCH_3)(Br)_2(CO)_2(4\text{-pic})]$ (**1**) and LiS₂CNPh₂

¹H NMR sample. A solution of LiS₂CNPh₂·0.60Et₂O (0.021 g, 0.072 mmol) in d₈-THF (0.50 ml) was added to a cold (–78 °C) slurry of **1a** (0.022 g, 0.035 mmol) in d₈-THF (0.25 ml). No reaction appeared to occur

at $-78\text{ }^{\circ}\text{C}$, and the stirred mixture was slowly warmed to $-30\text{ }^{\circ}\text{C}$. The cloudy, light orange solution was then cooled to $-78\text{ }^{\circ}\text{C}$ and quickly transferred at $-78\text{ }^{\circ}\text{C}$ to a NMR tube under N_2 . The tube was placed into an NMR probe at 233 K, and spectra were recorded after the probe was allowed to equilibrate at each temperature (233–333 K) for about 20 min. **3c**: δ 4.59 (br d, $J=8.08\text{ Hz}$, 1H, CH), 3.05 (m, 1H, CHMe), 2.26 (br s, 3H, CH_3 -pic), 2.03 (br d, $J=6.28\text{ Hz}$, 3H, CH_3). **4c**: δ 4.77 (br d, $J=8.84\text{ Hz}$, 1H, CH), 2.46 (br s, 3H, CH_3 -pic), 1.23 (br d, $J=5.31\text{ Hz}$, 3H, CH_3). **5c**: (273 K) δ 5.31 (d, $J=5.88\text{ Hz}$, 1H, CH), 3.10 (m, 1H, CHMe), 2.26 (d, $J=5.98\text{ Hz}$, 3H, CH_3). **6c**: (303 K) δ 3.51 (d, $J=8.98\text{ Hz}$, 1H, CH), 2.56 (m, 1H, CHMe), 2.02 (d, $J=6.11\text{ Hz}$, 3H, CH_3).

$[\text{W}(*\text{CO})_3(\text{CO})_3]$

The bottom of a 285 ml Schlenk flask containing a solution of $[\text{W}(\text{CO})_3\{(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2\}]$ (1.182 g, 2.679 mmol) in methylene chloride (20.0 ml) was placed in liquid nitrogen, and then ^{13}CO (Matheson, 99 at.% ^{13}C and *c.* 12 at.% ^{18}O , 255 ml, *c.* 10.43 mmol) was introduced into the evacuated flask at ambient pressure. The mixture was warmed to ambient temperature, and a 2.0 M aqueous solution of sulfuric acid (10.0 ml, 20.0 mmol) was added via syringe through a previously unpunctured septum. The hole in the septum was immediately plugged with stopcock grease, and the mixture was stirred vigorously for 17.5 h. The two phases were separated in air using a separatory funnel, and the aqueous phase was washed with methylene chloride ($3\times 5\text{ ml}$). The combined methylene chloride phases were dried over Na_2SO_4 for 20 min, and then filtered. The solution was cooled to $-78\text{ }^{\circ}\text{C}$ for 1 h, and then most of the supernatant was decanted away. The remaining methylene chloride was removed as follows: the mixture was placed at $-196\text{ }^{\circ}\text{C}$ into a Dewar vessel containing just a few ml of liquid nitrogen. The flask was attached to a $-78\text{ }^{\circ}\text{C}$ cold trap, and the methylene chloride slowly condensed into the $-78\text{ }^{\circ}\text{C}$ trap under vacuum as the mixture warmed. Both the supernatant and the distillate showed negligible $\nu(\text{CO})$ bands in their IR spectra and were discarded. The product was purified by sublimation to give white $\text{W}(*\text{CO})_6$ (0.641 g, 1.80 mmol, 67.4%). IR (CH_2Cl_2 , cm^{-1}): 1970 (m), 1940 (s, sh), 1930 (s), 1900 (m). The product was shown by mass spectroscopy to contain tungsten hexacarbonyl of molecular weight over the range 352–362, with an average molecular weight of 356.3.

$[\text{W}(*\text{CPhCHCHMe})\text{Br}_2(*\text{CO})_2(4\text{-picoline})]$ (**1'**)

This compound was prepared starting from $[\text{W}(*\text{CO})_6]$ ($\sim 50\%$ enriched with ^{13}C) following the procedure previously described for complex **1**.

$[\text{W}(\text{CPhCHCHMe})\text{Br}_2(*\text{CO})_2(4\text{-picoline})]$ (**1''**)

Complex **1** (0.180 g) was dissolved under N_2 in CH_2Cl_2 (9 ml) in a 50 ml round bottom Schlenk flask. Some of the solvent was pulled off under vacuum to remove all of the N_2 from the flask. The flask was then filled with ^{13}CO to $\frac{1}{2}$ atm above atmospheric pressure. The solution was heated to $45\text{ }^{\circ}\text{C}$ until the exchange was complete (6h, checked by IR). IR (CH_2Cl_2 , cm^{-1}): 1973 (m), 1894 (s). The sample was purified by chromatography on silica gel, using CH_2Cl_2 as the eluant. The collected brown fraction was reduced in volume to 2 ml. Upon slow addition of pentane (40 ml) a brown precipitate formed (0.102 g, 56.6%).

Crystallographic studies

Crystal structure of **2a**

A single crystal of $\text{C}_{22}\text{H}_{30}\text{N}_2\text{O}_2\text{S}_4\text{W}\cdot\text{CH}_2\text{Cl}_2$ measuring $0.14\times 0.20\times 0.48\text{ mm}$ was mounted on a glass fiber and centered on a Nicolet R3m diffractometer. Cell constants and their e.s.d.s were determined by a least-squares fit of 25 diffractometer-measured reflections with $14\leq 2\theta\leq 26^{\circ}$. The material belongs to the monoclinic crystal class, space group $P2_1/n$, with $a=10.406(2)$, $b=12.929(2)$, $c=21.658(4)\text{ \AA}$ and $\beta=94.30(2)^{\circ}$. A density of 1.72 g/cm^3 was calculated for $Z=4$, $FW=751.6\text{ g}$ and a unit cell volume of $2905.6(9)\text{ \AA}^3$.

All intensity measurements were made at low temperature ($180\pm 3\text{ K}$) using graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda=0.71069\text{ \AA}$) and an ω -scan technique with a variable scan rate of $3.91\text{--}29.3^{\circ}/\text{min}$. Background counts were taken for half the scan time at each extreme of the scan range. All data (4801) having $h, k\geq 0$ with $3\leq 2\theta\leq 50^{\circ}$ were measured in this manner. Crystal decomposition was monitored throughout data collection by remeasuring two standard reflections after every 50 data measurements; no significant variations were recorded. The intensities were reduced by applying Lorentz and polarization corrections. Empirical absorption corrections were applied based on the azimuthal scans of suitable reflections. Equivalent reflections were averaged to give 4278 unique data of which 3806 were considered to be observed [$|F_o|>3\sigma(F_o)$].

The structure was solved by standard heavy atom techniques. Following refinement of the non-hydrogen atoms of the complex with isotropic temperature factors, a difference map displayed three large peaks. These were assigned to a molecule solvent, methylene chloride. Subsequently, all non-hydrogen atoms were refined with anisotropic temperature factors after which difference maps showed peaks at plausible hydrogen positions. Hydrogen atoms were included in refinement in ideal positions (C–H 0.96 \AA , CCH 120 or 109.5°). In the final cycles of blocked-cascade least-squares refinement,

the non-hydrogen atoms were refined with anisotropic temperature factors and the hydrogens were varied using a riding model. Refinement converged (shift/error ≤ 0.2) at $R = 0.052$, $R_w = 0.055$. A final difference map displayed three residual peaks greater than $1.00 \text{ e}^-/\text{\AA}^3$, all in the vicinity of the tungsten atom. The quantity minimized by the least-squares program was $\Sigma w(|F_o| - |F_c|)^2$ where w is the weight of a given observation ($w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$, final value of $g = 0.00030$). The analytical forms for the scattering factors of the neutral atoms were used [8].

Crystal structure of 5a

A single crystal of $\text{C}_{22}\text{H}_{30}\text{N}_2\text{O}_2\text{S}_4\text{W}$ measuring $0.07 \times 0.10 \times 0.12 \text{ mm}$ was mounted on a glass fiber and centered on a Nicolet R3m diffractometer. Cell constants and their e.s.d.s were determined by a least-squares fit of 25 diffractometer-measured reflections with $20 \leq \theta \leq 25^\circ$. The material belongs to the triclinic crystal class, space group Pi, with $a = 9.236(3)$, $b = 11.116(3)$, $c = 13.771(4) \text{ \AA}$ and $\alpha = 96.13(2)$, $\beta = 100.66(2)$, $\gamma = 109.60(2)^\circ$. A density of 1.72 g/cm^3 was calculated for $Z = 2$, $FW = 666.7 \text{ g}$ and a unit cell volume of $1287(1) \text{ \AA}^3$.

All intensity measurements were made at low ($175 \pm 3 \text{ K}$) temperature using graphite-monochromated Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$) and an ω -scan technique with a variable scan rate of $3.91\text{--}29.30^\circ/\text{min}$. Background counts were taken for half the scan time at each extreme of the scan range. All data (4733) having $I \geq 0$ with $3 \leq 2\theta \leq 50^\circ$ were measured in this manner. Crystal decomposition was monitored throughout data collection by remeasuring two standard reflections after every 50 data measurements; no significant variations in intensity were observed. The intensities were reduced by applying Lorentz, polarization and decay corrections. Empirical absorption corrections were made based on the azimuthal scans of 16 reflections with χ near 270° . Systematically absent reflections were eliminated and equivalent reflections were averaged to give 4526 unique data of which 3865 were considered to be observed [$|F_o| > 3\sigma(F_o)$].

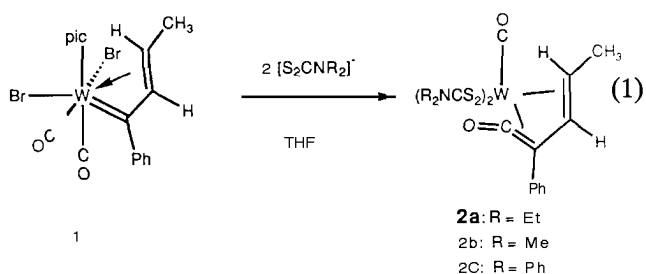
The structure was solved using a Patterson map. All hydrogen atoms were included in refinement at idealized positions (C-H 0.96 \AA , CCH 120 or 109.5°). In the final cycles of blocked-cascade least-squares refinement, the non-hydrogen atoms were refined with anisotropic temperature factors and the hydrogen atoms were varied using a riding model. Refinement converged (shift/error ≤ 0.15) at $R = 0.052$, $R_w = 0.049$. The two largest peaks in a final difference map (max $\text{e}^-/\text{\AA}^3 = 3.0$) were in the vicinity of the tungsten atom. The quantity minimized by the least-squares program was $\Sigma w(|F_o| - |F_c|)^2$ where w is the weight of a given observation ($w^{-1} = \Sigma^2(|F_o|) + g|F_o|^2$, final value of

$g = 0.00105$). The analytical forms for the scattering factors of the neutral atoms were used [7].

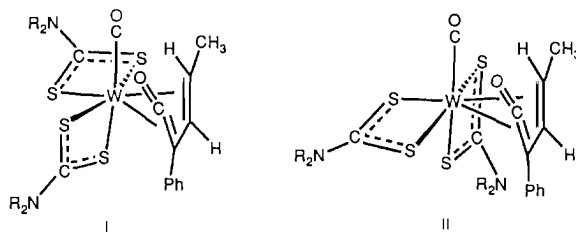
Results and discussion

Synthesis and characterization of the vinylketene complexes 2a-c

When two equivalents of sodium diethyldithiocarbamate are added at room temperature to a brown slurry of the tungsten allylidene complex $[\text{W}(\text{CPhCHCHMe})\text{Br}_2(\text{CO})_2(4\text{-picoline})]$ (1) in THF, an orange-red cloudy solution forms very rapidly (eqn. (1)). The IR spectrum of the reaction solution taken



within a minute exhibits two IR absorptions in the metal carbonyl region at 1937 and 1854 cm^{-1} , which slowly give way to a single absorption at 1936 cm^{-1} . This indicates that initially a tungsten complex containing two carbonyl ligands forms which slowly transforms into the final product containing only one carbonyl ligand. At 50°C , the reaction is complete in about 1 h. The product was characterized as the vinylketene complex 2a. Similarly, complexes 2b and 2c were obtained by using sodium dimethyldithiocarbamate and lithium diphenyldithiocarbamate, respectively. The ^1H NMR spectra of the isolated products reveal that all three complexes exist as mixtures of two isomers (2a: 87:13; 2b: 87:13; 2c: 95:5). The two isomers presumably arise from the two possible arrangements of the chelating dithiocarbamate ligands as shown below in I and II. Whether I or II represents the major isomer has not been determined. The four ^{13}C NMR resonances of the contact carbon atoms of the vinylketene ligand of 2a (major isomer) are located at $\delta 234.9$ (C=O), 79.4 (CH), 68.9 (CHMe) and 56.1 (CPh). The resonance of the carbonyl ligand was observed at $\delta 214.5$, the two resonances of the dithiocarbamate carbon atoms at $\delta 214.1$ and 204.7 . The respective ^{13}C NMR resonances of complexes 2b,c are similar to those of 2a.



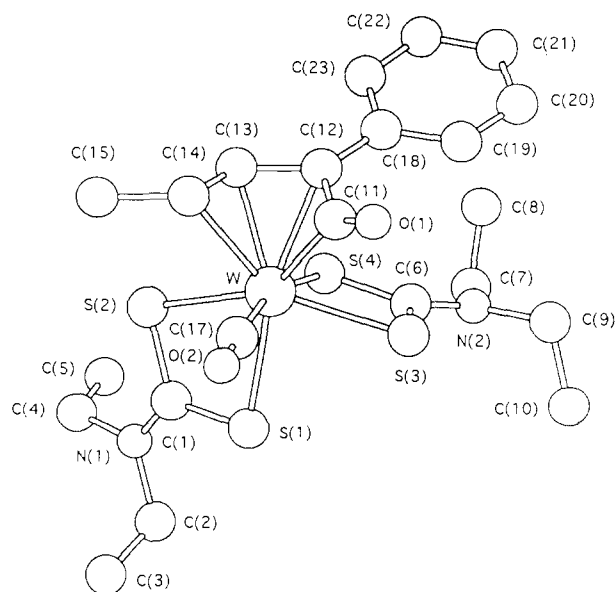
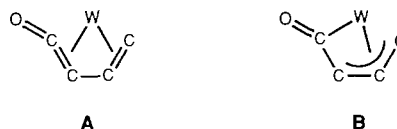


Fig. 1. Molecular structure of **2a**.

Solid state structure of complex **2a**

The solid state structure of **2a** (isomer **I**) was determined by X-ray crystallography. The molecular structure is shown in Fig. 1. Crystal data are collected in Table 1. Final atomic positional parameters are shown in Table 2, selected bond distances and bond angles are listed in Table 3. The bond distances between tungsten and the four contact atoms of the vinylketene

ligand are W–C(11) 2.193(11), W–C(12) 2.360(12), W–C(13) 2.260(12), and W–C(14) 2.391(13) Å. The C(11)–C(12) bond, 1.43(2) Å, and the C(13)–C(14) bond, 1.35(2) Å, are both shorter than the C(12)–C(13) bond, 1.49(2) Å. The bonding of the ligand has thus more vinylketene character, **A**, than allylacyl character, **B**. In some other vinylketene metal complexes, in particular those of the Fe(CO)₃ fragment, the allylacyl character is strongly pronounced [2a,c, 6a,c,e,f].



Course of formation of complexes **2a–c**

To learn more about the dithiocarbamate-induced allylidene–carbonyl coupling, the course of formation of complexes **2a–c** was followed by NMR spectroscopy. The NMR samples of the reaction mixtures were prepared at low temperatures in d₈-THF, and the ¹H NMR spectra of the samples were recorded at increasing temperatures and suitable time intervals. The temperature/time course of the formation of complexes **2a–c** is shown in Fig. 2. In all three cases, four intermediates were discerned, **3a–c**, **4a–c**, **5a–c** and **6a–c**. In the case of formation of **2a**, for example, two intermediates, **3a** and **4a**, which both still contain co-

TABLE 1. Crystallographic data for complexes **2a** and **5a**

	2a	5a
<i>Crystal parameters</i>		
Formula	C ₂₂ H ₃₀ N ₂ O ₂ S ₄ W · CH ₂ Cl ₂	C ₂₂ H ₃₀ N ₂ O ₂ S ₄ W
Space group	P2 ₁ /n	P1
<i>a</i> (Å)	10.406(2)	9.236(3)
<i>b</i> (Å)	12.929(2)	11.116(3)
<i>c</i> (Å)	21.658(4)	13.771(4)
α (°)		96.13(2)
β (°)	94.30(2)	100.66(2)
γ (°)		109.60(2)
<i>V</i> (Å ³)	2905.6(9)	1287(1)
<i>Z</i>	4	2
<i>D</i> _{calc} (g cm ⁻³)	1.72	1.72
Color	red	red–orange
Size (mm)	0.14 × 0.20 × 0.48	0.07 × 0.10 × 0.12
<i>Data collection and refinement</i>		
Diffractometer	Nicolet R3m	Nicolet R3m
Temperature (K)	180	175
Radiation	Mo K α	Mo K α
Monochromator	graphite single crystal	graphite single crystal
Scan limits (°)	3 < 2 θ < 50	3 < 2 θ < 50
Observed reflections	3806	3865
Parameters	307	280
<i>R</i> (<i>F</i>)	0.052	0.052
<i>R</i> _w (<i>F</i>)	0.055	0.049

TABLE 2. Final atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) of **2a**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ^a
W	2064(1)	1951(1)	1489(1)	28(1)*
S(1)	1180(3)	1179(2)	472(1)	38(1)*
S(2)	1015(3)	3316(2)	770(1)	35(1)*
C(1)	823(11)	2404(10)	187(6)	32(4)*
N(1)	414(11)	2625(8)	-372(5)	39(4)*
C(2)	221(16)	1805(10)	-873(6)	49(5)*
C(3)	-1077(15)	1538(14)	-1024(7)	59(6)*
C(4)	243(17)	3683(11)	-592(7)	61(6)*
C(5)	1410(14)	4211(12)	-750(6)	51(5)*
S(3)	3565(3)	452(2)	1442(1)	35(1)*
S(4)	4001(3)	2441(2)	902(1)	35(1)*
C(6)	4620(12)	1238(9)	1077(5)	32(4)*
N(2)	5774(11)	922(9)	930(5)	42(4)*
C(7)	6627(16)	1588(12)	552(7)	59(6)*
C(8)	7445(15)	2296(13)	974(8)	59(6)*
C(9)	6329(15)	-67(11)	1168(7)	56(6)*
C(10)	6069(18)	-931(14)	682(8)	76(7)*
C(11)	2678(13)	1535(9)	2448(5)	33(4)*
C(12)	3386(14)	2465(9)	2368(5)	36(5)*
C(13)	2452(11)	3288(9)	2149(5)	31(4)*
C(14)	1196(14)	3088(9)	2223(6)	40(4)*
C(15)	88(14)	3870(9)	2043(6)	41(5)*
O(1)	2621(9)	852(7)	2819(4)	42(3)*
C(17)	489(13)	1217(9)	1781(6)	37(4)*
O(2)	-335(9)	779(7)	1932(4)	49(3)*
C(18)	4768(12)	2552(9)	2455(5)	28(4)*
C(19)	5533(14)	1676(10)	2607(6)	42(5)*
C(20)	6827(12)	1755(10)	2697(6)	40(5)*
C(21)	7429(14)	2710(11)	2693(6)	45(5)*
C(22)	6711(16)	3575(11)	2549(6)	59(6)*
C(23)	5393(12)	3481(11)	2441(5)	34(5)*
C(25)	4087(19)	5360(14)	942(9)	79(7)*
Cl(1)	3545(8)	6032(6)	282(3)	137(3)*
Cl(2)	5240(7)	6019(8)	1381(4)	151(4)*

^aStarred items: equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

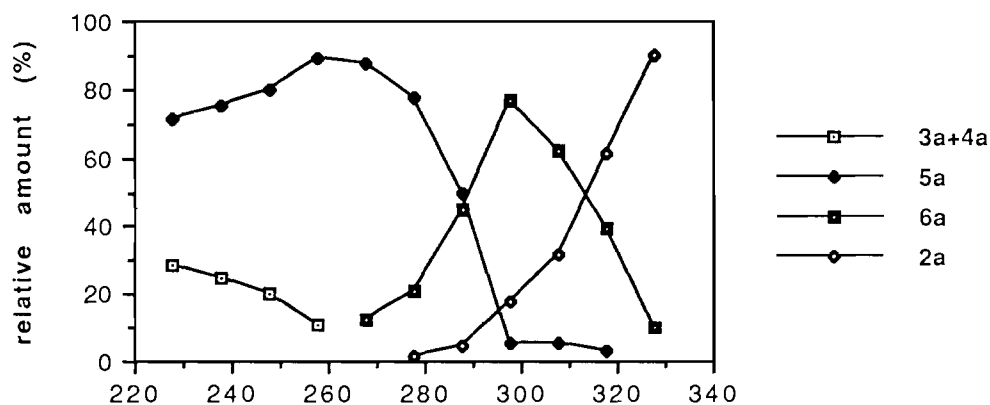
ordinated 4-picoline, are present at temperatures below -15 °C. Even at low temperatures, a third intermediate, **5a**, begins to form and is present up to room temperature. Approximately when the maximum concentration of **5a** is reached, a fourth intermediate, **6a**, begins to build up in significant concentrations. At temperatures above 0 °C, with both **5a** and **6a** present in the reaction solution, the final product **2a** forms as its mixture of isomers.

¹³C NMR spectroscopic investigation of reaction intermediates

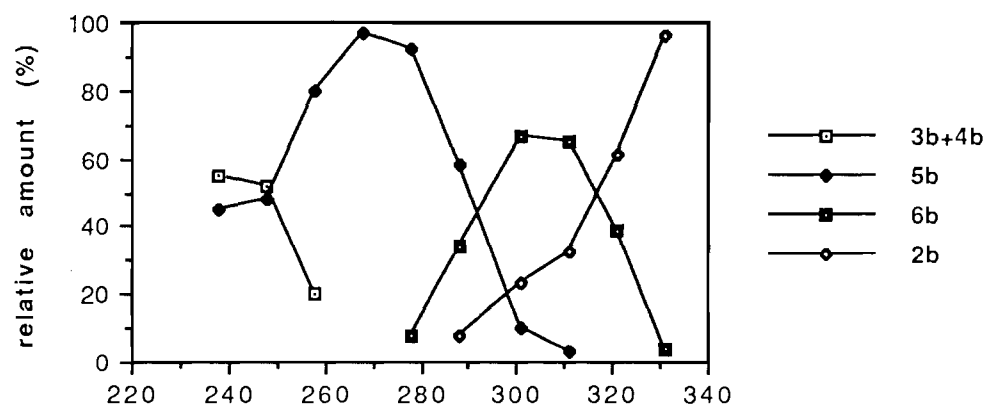
The ¹³C NMR spectra of the intermediates **3a–6a** do not exhibit resonances at fields lower than δ 232, indicating that the vinylcarbene unit may be in a different bonding environment than in complex **1**. (All resonances between δ 232 and 200 can be accounted for by the carbonyl and dithiocarbamate ligands. The signal of

TABLE 3. Selected bond distances and bond angles for **2a**

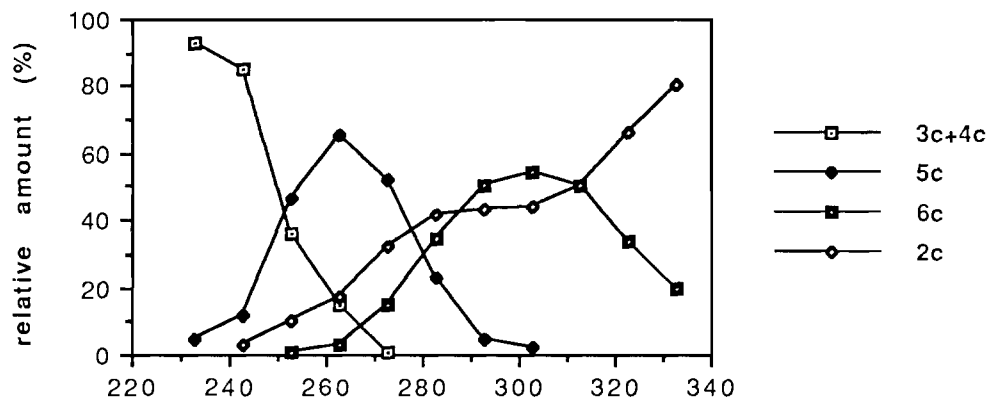
Bond distances (Å)			
W–S(1)	2.527(3)	W–S(2)	2.544(3)
W–S(3)	2.496(3)	W–S(4)	2.543(3)
W–C(11)	2.193(11)	W–C(12)	2.360(12)
W–C(13)	2.260(12)	W–C(14)	2.391(13)
W–C(17)	2.035(13)	S(1)–C(1)	1.731(13)
S(2)–C(1)	1.729(13)	C(1)–N(1)	1.28(2)
N(1)–C(2)	1.52(2)	N(1)–C(4)	1.45(2)
C(2)–C(3)	1.41(2)	C(4)–C(5)	1.46(2)
S(3)–C(6)	1.730(13)	S(4)–C(6)	1.714(12)
C(6)–N(2)	1.33(2)	N(2)–C(7)	1.52(2)
N(2)–C(9)	1.48(2)	C(7)–C(8)	1.51(2)
C(9)–C(10)	1.55(2)	C(11)–C(12)	1.43(2)
C(11)–O(1)	1.198(14)	C(12)–C(13)	1.49(2)
C(12)–C(18)	1.44(2)	C(13)–C(14)	1.35(2)
C(14)–C(15)	1.56(2)	C(17)–O(2)	1.10(2)
C(18)–C(19)	1.41(2)	C(18)–C(23)	1.37(2)
C(19)–C(20)	1.35(2)	C(20)–C(21)	1.38(2)
C(21)–C(22)	1.37(2)	C(22)–C(23)	1.38(2)
C(25)–Cl(1)	1.73(2)	C(25)–Cl(2)	1.70(2)
Bond angles (°)			
S(1)–W–S(2)	68.3(1)	S(1)–W–S(3)	81.1(1)
S(2)–W–S(3)	139.0(1)	S(1)–W–S(4)	85.0(1)
S(2)–W–S(4)	80.9(1)	S(3)–W–S(4)	69.6(1)
S(1)–W–C(11)	142.1(3)	S(2)–W–C(11)	146.2(3)
S(3)–W–C(11)	73.1(3)	S(4)–W–C(11)	110.4(4)
S(1)–W–C(12)	165.1(3)	S(2)–W–C(12)	119.7(3)
S(3)–W–C(12)	85.6(3)	S(4)–W–C(12)	84.1(3)
C(11)–W–C(12)	36.3(4)	S(1)–W–C(13)	152.8(3)
S(2)–W–C(13)	84.6(3)	S(3)–W–C(13)	122.5(3)
S(4)–W–C(13)	90.8(3)	C(11)–W–C(13)	64.1(4)
C(12)–W–C(13)	37.7(4)	S(1)–W–C(14)	133.7(3)
S(2)–W–C(14)	79.3(3)	S(3)–W–C(14)	140.7(3)
S(4)–W–C(14)	122.2(3)	C(11)–W–C(14)	67.6(4)
C(12)–W–C(14)	61.1(5)	C(13)–W–C(14)	33.7(4)
S(1)–W–C(17)	80.6(3)	S(2)–W–C(17)	101.2(3)
S(3)–W–C(17)	99.9(3)	S(4)–W–C(17)	163.4(3)
C(11)–W–C(17)	77.1(5)	C(12)–W–C(17)	108.4(5)
C(13)–W–C(17)	105.7(5)	C(14)–W–C(17)	74.2(5)
W–S(1)–C(1)	90.2(4)	W–S(2)–C(1)	89.7(4)
S(1)–C(1)–S(2)	110.6(7)	S(1)–C(1)–N(1)	126.0(10)
S(2)–C(1)–N(1)	123.3(10)	C(1)–N(1)–C(2)	122.3(11)
C(1)–N(1)–C(4)	122.7(11)	C(2)–N(1)–C(4)	114.6(10)
N(1)–C(2)–C(3)	114.2(13)	N(1)–C(4)–C(5)	115.7(13)
W–S(3)–C(6)	89.0(4)	W–S(4)–C(6)	87.8(4)
S(3)–C(6)–S(4)	113.2(7)	S(3)–C(6)–N(2)	123.0(9)
S(4)–C(6)–N(2)	123.8(10)	C(6)–N(2)–C(7)	121.9(11)
C(6)–N(2)–C(9)	121.2(11)	C(7)–N(2)–C(9)	116.7(11)
N(2)–C(7)–C(8)	110.1(12)	N(2)–C(9)–C(10)	110.0(12)
W–C(11)–C(12)	78.2(7)	W–C(11)–O(1)	142.2(9)
C(12)–C(11)–O(1)	138.9(12)	W–C(12)–C(11)	65.5(6)
W–C(12)–C(13)	67.5(6)	C(11)–C(12)–C(13)	108.0(11)
W–C(12)–C(18)	130.0(8)	C(11)–C(12)–C(18)	124.6(11)
C(13)–C(12)–C(18)	127.2(11)	W–C(13)–C(12)	74.8(7)
W–C(13)–C(14)	78.5(7)	C(12)–C(13)–C(14)	115.9(11)
W–C(14)–C(13)	67.9(7)	W–C(14)–C(15)	122.8(8)
C(13)–C(14)–C(15)	123.3(11)	W–C(17)–O(2)	176.8(11)
C(12)–C(18)–C(19)	120.6(11)	C(12)–C(18)–C(23)	122.5(11)
C(19)–C(18)–C(23)	116.7(12)	C(18)–C(19)–C(20)	120.9(12)
C(19)–C(20)–C(21)	120.9(12)	C(20)–C(21)–C(22)	119.4(13)
C(21)–C(22)–C(23)	119.0(14)	C(18)–C(23)–C(22)	122.9(13)
Cl(1)–C(25)–Cl(2)	112.5(11)		



(a) Temperature (K)



(b) Temperature (K)

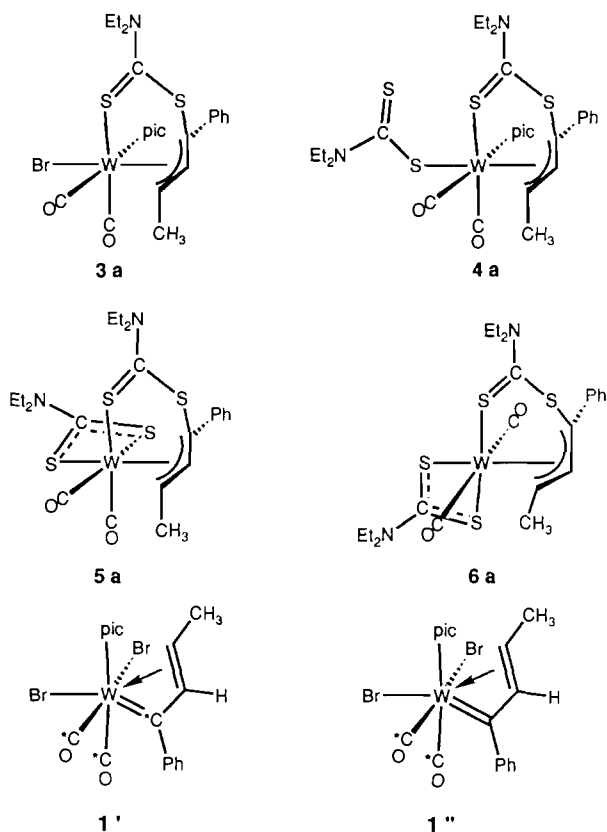


(c) Temperature (K)

Fig. 2. The course of formation of formation of complexes **2a** (a), **2b** (b) and **2c** (c) with increasing temperature. 100% represents the sum of all components. The samples were kept for about 20 min at each temperature.

the vinylcarbene carbon atom in **1** appears at δ 240.) The studies described below show that complexes **5a** and **6a** contain η^4 -allyldithiocarbamate ligands. Even though the quality of the ^{13}C NMR spectrum of the sample containing the less accessible intermediates **3a** and **4a** was of poor quality (i.e. weak signals at low

field may have been missed), we propose that complexes **3a** and **4a** also contain allyldithiocarbamate ligands. Possible structural formulas for complexes **3a** and **4a** are shown below. The nature of the more accessible intermediates **5a** and **6a** was probed in considerable detail by identifying the ^{13}C NMR signals originating



from the carbonyl and carbene carbon atoms. This was achieved by using $[\text{W}(*\text{CPhCHCHMe})\text{Br}_2(*\text{CO})_2(4\text{-pic})]$ (**1'**) prepared from $[\text{W}(*\text{CO})_6]$ ($\sim 50\%$ enriched, the asterisk denotes the presence of ^{13}C), as the starting material [3]. To distinguish between the signals originating from the carbonyl ligands from those originating from the carbene carbon atom, the carbonyl ligands in **1** were exchanged by heating **1** in d_8 -THF under an atmosphere of $*\text{CO}$ to give $[\text{W}(\text{CPhCHCHMe})\text{Br}_2(*\text{CO})_2(4\text{-pic})]$ (**1''**). The results show that the CPh carbon atom resonates at δ 73.8 in compound **5a** and at δ 63.7 in compound **6a**. The carbonyl carbon atoms in **5a** give rise to signals at δ 231.5 and 224.6, those in **6a** to signals at δ 223.7 and 221.4. In compound **5a** the signals of the carbonyl carbon atoms exhibit no observable coupling to each other or to the CPh carbon atom. In compound **6a**, a coupling between the carbonyl carbon atoms with $J=7.5$ Hz is observed. The carbonyl signal of compound **6a** at δ 223.7 also exhibits a small coupling (not fully resolved) to the CPh carbon atom. The signals of the CH and CHMe atoms of the vinyl group appear at δ 71.3 and 56.2 for **5a** and at δ 70.4 and 63.7 for **6a**. Based on the available spectroscopic information, complexes **5a** and **6a** contain the same type of allyldithiocarbamate ligand (see below). The observation of coupling between the two carbonyl carbon atoms in **6a** suggests a *trans* orientation of the two carbonyl ligands [9]. The fact that the chemical shifts

of the carbonyl carbon resonances of **6a** are at slightly higher field than those of **5a** also points towards a *trans* arrangement of the carbonyl ligands. In mutual *trans* orientation, the carbonyl ligands sense less electron density on the metal center due to competition for π backbonding [10]. It is not clear, however, which factors would favor the *trans* orientation of the carbonyl ligands in intermediate **6a**. Unfortunately, in the IR spectrum of the reaction solution there are no absorptions which could unambiguously be assigned to **6a**. The carbonyl absorptions of **6a** are either very similar to those of **5a**, which would indicate that the two carbonyl ligands are oriented *cis* to each other, or the compound gives rise to a strong absorption near 1936 cm^{-1} , where both **5a** and **2a** have an absorption. If the carbonyl ligands in **6a** are in *cis* positions, then **5a** and **6a** could differ from each other by the orientation of the allyl portion of the allyldithiocarbamate ligand. It is doubtful, however, whether a 'flip' (i.e. rotation about the C(4)–C(5) bond) of the allyl group would exert such a pronounced effect on the chemical shift as well as the coupling of the carbonyl carbon atoms. We favor therefore a structure of **6a** in which the carbonyl ligands are in mutual *trans* positions. A possible structure for **6a** is shown above.

Isolation and solid state structure of intermediate **5a**

From the variable temperature NMR study of the course of the formation of **2a** we had learned that at $-15\text{ }^\circ\text{C}$ intermediate **5a** is almost the sole species in the reaction solution. Based on this information it was possible to prepare a sample of **5a**, which was further purified by column chromatography (silica/ CH_2Cl_2) at

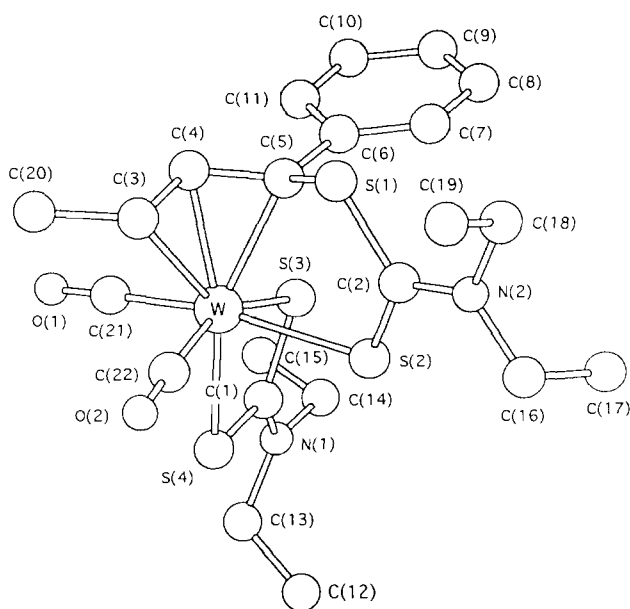


Fig. 3. Molecular structure of **5a**.

TABLE 4. Final atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) of **5a**

	x	y	z	U^a
W	50(1)	2359(1)	2059(1)	23(1)*
S(1)	-3145(3)	3238(2)	1555(2)	31(1)*
S(2)	-932(3)	3293(3)	3456(2)	32(1)*
S(3)	-764(3)	215(2)	2777(2)	32(1)*
S(4)	2265(3)	2317(2)	3422(2)	32(1)*
N(1)	1694(9)	75(8)	4102(6)	33(3)*
N(2)	-3014(9)	4483(7)	3332(6)	30(3)*
C(1)	1132(11)	765(9)	3498(7)	29(4)*
C(2)	-2393(11)	3751(9)	2856(7)	39(4)*
C(3)	-520(12)	3141(10)	557(8)	35(4)*
C(4)	-1657(11)	1907(10)	593(7)	31(4)*
C(5)	-2556(11)	1866(9)	1332(7)	26(3)*
C(6)	-3734(11)	613(9)	1440(7)	26(3)*
C(7)	-4853(12)	571(11)	1989(8)	40(4)*
C(8)	-5957(14)	-597(11)	2073(9)	48(5)*
C(9)	-5983(13)	-1755(11)	1589(9)	46(5)*
C(10)	-4887(13)	-1737(10)	1021(8)	43(4)*
C(11)	-3774(12)	-568(10)	952(8)	36(4)*
C(12)	3675(13)	1364(13)	5662(8)	49(5)*
C(13)	3349(11)	545(11)	4639(7)	35(4)*
C(14)	690(12)	-1237(10)	4203(8)	37(4)*
C(15)	798(14)	-2294(10)	3457(11)	53(5)*
C(16)	-2402(13)	5017(10)	4406(8)	39(4)*
C(17)	-3256(15)	4133(12)	5045(9)	50(5)*
C(18)	-4333(12)	4812(10)	2819(8)	36(4)*
C(19)	-3814(17)	5970(12)	2317(10)	57(6)*
C(20)	470(15)	3246(13)	-223(9)	52(6)*
C(21)	1110(12)	1491(10)	1264(8)	34(4)*
C(22)	1317(12)	4159(11)	2092(8)	38(4)*
O(1)	1728(11)	937(10)	841(7)	64(4)*
O(2)	2088(10)	5253(7)	2139(7)	59(4)*

*Starred items: equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

-25 °C. Crystals suitable for X-ray crystallography were obtained by cooling a solution of **5a** in CH_2Cl_2 /pentane from -15 to -78 °C. The molecular structure of **5a** is shown in Fig. 3. Crystal data are collected in Table 1. Final atomic positional parameters are shown in Table 4, selected bond distances and bond angles are listed in Table 5. The structure reveals the true nature of intermediate **5a**. The former allylidene ligand is transformed into an allyl ligand by the addition of dithiocarbamate across the metal-carbon double bond. The bond distances between tungsten and the allyl carbon atoms, W-C(3) 2.366(11), W-C(4) 2.211 and W-C(5) 2.281 Å, are within the range found for other allyl tungsten complexes [11].

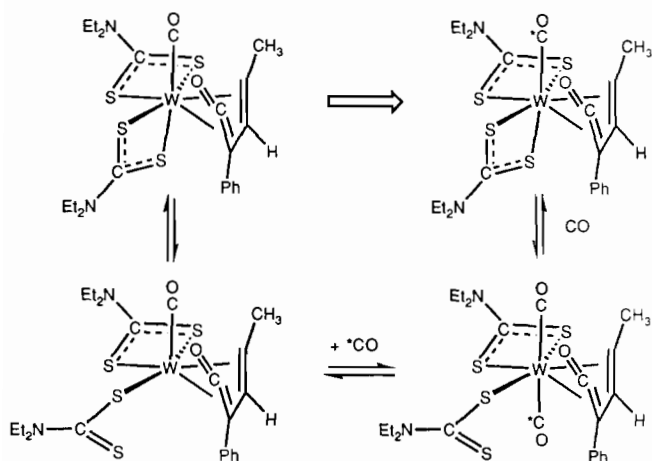
Carbonyl exchange in complex **2a**

When complex **2a** is heated in d_8 -THF under an atmosphere of $^*\text{CO}$, the labeled carbon monoxide is incorporated simultaneously into both carbonyl positions, namely the carbonyl ligand and the ketyl carbonyl group. The allylidene-carbonyl coupling is thus

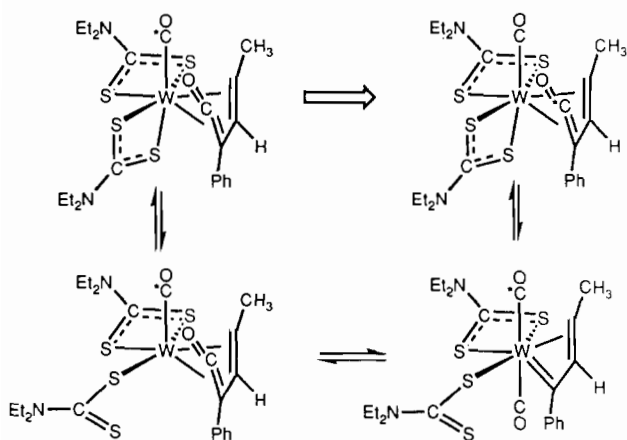
TABLE 5. Selected bond distances and bond angles for **5a**

Bond distance (Å)			
W-S(2)	2.540(3)	W-S(3)	2.608(3)
W-S(4)	2.524(3)	W-C(3)	2.366(11)
W-C(4)	2.211(9)	W-C(5)	2.281(9)
W-C(21)	1.974(12)	W-C(22)	1.941(11)
S(1)-C(2)	1.754(10)	S(1)-C(5)	1.799(11)
S(2)-C(2)	1.703(11)	S(3)-C(1)	1.713(9)
S(4)-C(1)	1.717(9)	N(1)-C(1)	1.340(14)
N(1)-C(13)	1.456(12)	N(1)-C(14)	1.480(13)
N(2)-C(2)	1.326(15)	N(2)-C(16)	1.462(13)
N(2)-C(18)	1.467(15)	C(3)-C(4)	1.433(13)
C(3)-C(20)	1.523(18)	C(4)-C(5)	1.423(15)
C(5)-C(6)	1.495(12)	C(6)-C(7)	1.380(17)
C(6)-C(11)	1.395(15)	C(7)-C(8)	1.388(15)
C(8)-C(9)	1.376(18)	C(9)-C(10)	1.386(19)
C(10)-C(11)	1.386(14)	C(12)-C(13)	1.513(15)
C(14)-C(15)	1.518(18)	C(16)-C(17)	1.511(17)
C(18)-C(19)	1.505(18)	C(21)-O(1)	1.151(17)
C(22)-O(2)	1.173(13)		
Bond angles (°)			
S(2)-W-S(3)	86.0(1)	S(2)-W-S(4)	86.7(1)
S(3)-W-S(4)	68.4(1)	S(2)-W-C(3)	112.1(3)
S(3)-W-C(3)	140.1(2)	S(4)-W-C(3)	143.8(3)
S(2)-W-C(4)	111.2(3)	S(3)-W-C(4)	104.6(3)
S(4)-W-C(4)	160.7(3)	C(3)-W-C(4)	36.3(3)
S(3)-W-C(5)	77.3(3)	S(3)-W-C(5)	88.4(2)
S(4)-W-C(5)	152.8(3)	C(3)-W-C(5)	63.4(4)
C(4)-W-C(5)	36.9(4)	S(2)-W-C(21)	165.1(3)
S(3)-W-C(21)	84.3(3)	S(4)-W-C(21)	79.2(3)
C(3)-W-C(21)	82.5(4)	C(4)-W-C(21)	82.3(4)
C(5)-W-C(21)	113.6(4)	S(2)-W-C(22)	84.4(4)
S(3)-W-C(22)	154.6(3)	S(4)-W-C(22)	87.6(3)
C(3)-W-C(22)	65.1(4)	C(4)-W-C(22)	100.8(4)
C(5)-W-C(22)	112.2(4)	C(21)-W-C(22)	99.7(5)
C(2)-S(1)-C(5)	101.3(5)	W-S(2)-C(2)	104.9(4)
W-S(3)-C(1)	87.0(4)	W-S(4)-C(1)	89.7(3)
C(1)-N(1)-C(13)	121.4(8)	C(1)-N(1)-C(14)	121.6(8)
C(13)-N(1)-C(14)	116.8(9)	C(2)-N(2)-C(16)	121.3(9)
C(2)-N(2)-C(18)	122.5(8)	C(16)-N(2)-C(18)	116.2(9)
S(3)-C(1)-S(4)	114.6(6)	S(3)-C(1)-N(1)	123.6(7)
S(4)-C(1)-N(1)	121.8(6)	S(1)-C(2)-S(2)	119.8(7)
S(1)-C(2)-N(2)	117.4(6)	S(2)-C(2)-N(2)	122.8(7)
W-C(3)-C(4)	66.0(6)	W-C(3)-C(20)	123.1(9)
C(4)-C(3)-C(20)	119.9(10)	W-C(4)-C(3)	77.8(5)
W-C(4)-C(5)	74.2(5)	C(3)-C(4)-C(5)	117.5(9)
W-C(5)-S(1)	111.7(4)	W-C(5)-C(4)	68.9(5)
S(1)-C(5)-C(4)	115.4(8)	W-C(5)-C(6)	118.6(7)
S(1)-C(5)-C(6)	113.8(8)	C(4)-C(5)-C(6)	121.0(8)
W-H(5)-C(5)	134.4(4)	C(5)-C(6)-C(7)	122.1(9)
C(5)-C(6)-C(11)	120.5(10)	C(7)-C(6)-C(11)	117.4(9)
C(6)-C(7)-C(8)	121.7(11)	C(7)-C(8)-C(9)	120.4(12)
C(8)-C(9)-C(10)	119.0(10)	C(9)-C(10)-C(11)	120.2(11)
C(6)-C(11)-C(10)	121.3(11)	N(1)-C(13)-C(12)	113.2(10)
N(1)-C(14)-C(15)	112.0(10)	N(2)-C(16)-C(17)	112.3(7)
N(2)-C(18)-C(19)	113.3(9)	W-C(21)-O(1)	176.0(10)
W-C(22)-O(2)	178.2(10)		

a reversible process [2i, 6b,c]. The carbonyl exchange process is probably initiated by an η^2 - η^1 conversion of a dithiocarbamate ligand in **2a**. Labeled carbon



Scheme 1.



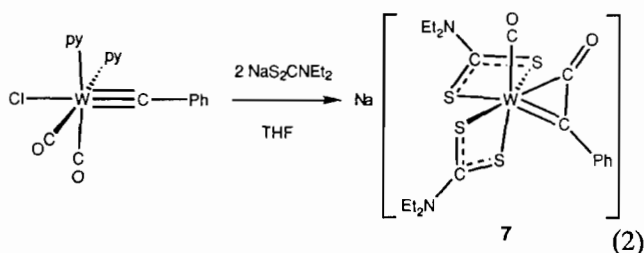
Scheme 2.

monoxide could then coordinate to the open site, followed by dissociation of the non-labeled carbon monoxide and recoordination of the pending arm of the dithiocarbamate ligand (Scheme 1). Alternatively, the empty coordination site generated by the η^2 - η^1 conversion of a dithiocarbamate ligand could be followed by a vinylketene cleavage to regenerate allylidene and carbon monoxide ligands (Scheme 2). If this event occurs in a complex in which the carbonyl ligand had prior been exchanged, recoupling could then occur with the labeled carbonyl ligand, thus leading to a labeled vinylketene ligand.

Conclusions

The present study shows that the mechanism of dithiocarbamate-induced vinylcarbene-carbonyl coupling in complex **1** proceeds via at least four discrete intermediates **3-6**. All intermediates are proposed to contain η^4 -allyldithiocarbamate ligands. The addition

of dithiocarbamate across the metal-carbon double bond may be understood as a nucleophilic attack at the carbene carbon atom. Attack of nucleophiles at the related allylidene complex $[\text{W}(\text{CPhCPhCHTol})(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]^+\text{BF}_4^-$ was previously reported by Geoffroy and co-workers [12]. Formation of the vinylketene ligand requires cleavage of the carbon-sulfur bond in the η^4 -allyldithiocarbamate ligand. It seems reasonable to assume that the allyldithiocarbamate ligand cleaves into allylidene and dithiocarbamate units, possibly an η^3 -allylidene and an η^1 -dithiocarbamate ligand. Chelation of the dithiocarbamate ligand could then induce the carbon-carbon bond-forming step, i.e. the allylidene-carbonyl coupling. The last step in Scheme 2 could serve as a representation of this coupling step. The coupling reaction of the present study is reminiscent of the dithiocarbamate-induced coupling of alkylidyne and carbonyl ligands in the reaction of complexes of the type $[\text{W}(\text{CR})\text{Cl}(\text{CO})_2(\text{pyridine})_2]$ with dithiocarbamates to give ketenyl complexes, e.g. **7** (eqn. (2)) [13].



There is a significant amount of experimental evidence suggesting that an increase of the electron density at the metal center facilitates the alkylidyne-carbonyl coupling step [14]. The build up of electron density in complex **1** by the addition of dithiocarbamate ligands may play a similar role in the formation of complexes **2**. A test of this proposal, however, will have to wait until a suitable variety of vinylcarbene carbonylmetal complexes, which undergo vinylcarbene-carbonyl coupling, becomes available.

Supplementary material

Further details of the crystal structure investigation of **5a** may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-58260, the names of the authors, and the journal citation.

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