Stepwise Incorporation of a Carbyne Ligand into Vinylcarbene and Vinylketene Ligands at a Tungsten Center

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Transition-metal vinlycarbene, or allylidene, complexes have recently attracted considerable attention as reagents and intermediates in organometallic reactions.[1-10] Vinylcarbene ligands may form by coupling of carbene and alkyne ligands,[4] and such steps have been postulated to occur in acetylene polymerization,[5] in the formation of naphthols from alkoxy(phenylcarbene)-pentacarbonylchromium complexes and alkynes,[6] and in related reactions.[7,8] Some of these processes also involve a further coupling of intermediate vinylcarbene ligands and carbonyl ligands resulting in coordinated vinlyketenes.[2,6,8-10] The detailed study of these fundamental carbon–carbon bond-forming steps requires the synthesis of transition-metal complexes containing the requisite ligand combinations. We have previously prepared stable tungsten carbene alkyne complexes,[11] and here we wish to report the synthesis of a novel type of tungsten vinylcarbene complex from the reaction of a tungsten carbyne complex and an allyl halide and the subsequent induction of carbonyl–vinylcarbene coupling to give a tungsten vinylketene complex.

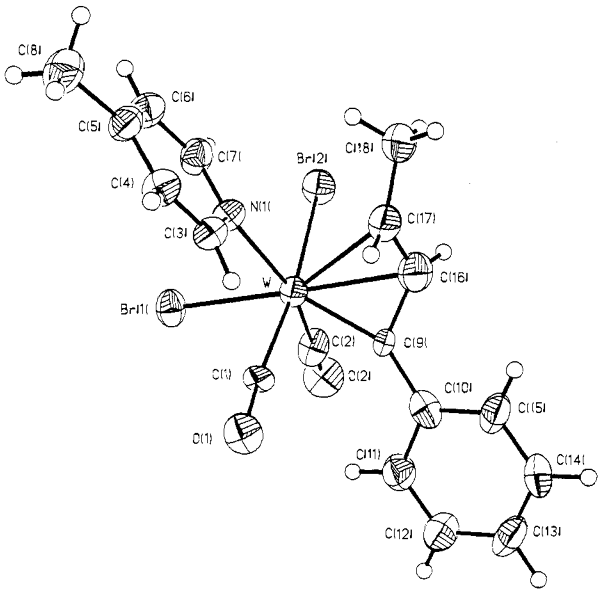


Figure 1. Molecular structure of complex **2**. W–Br(1), 2.599 (2); W–Br(2), 2.614 (2); W–N(1), 2.28 (1); W–C(1), 1.98 (2); W–C(2), 1.99 (2); W–C(9), 1.98 (2); W–C(16), 2.38 (2); W–C(17), 2.60 (2); C(9)–C(16), 1.44 (2); C(16)–C(17), 1.35 (1) Å. W–C(9)–C(10), 149 (1)°; W–C(9)–C(16), 87.1 (9)°; C(9)–C(16)–C(17), 122 (2)°; C(16)–C-(17)–C(18), 127 (2)°.

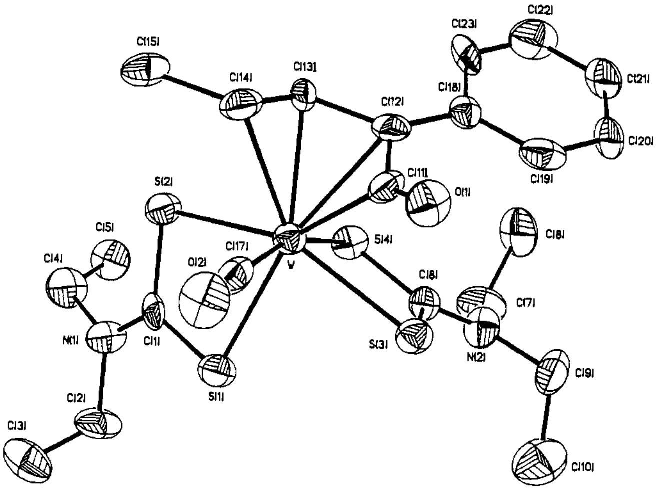
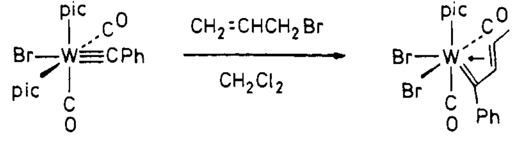
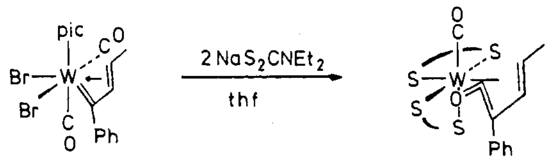


Figure 2. Molecular structure of complex **4**. W–C(11), 2.193 (11); W–C(12), 2.360 (12); W–C(13), 2.260 (12); W–C(14), 2.391 (13); W–C(17), 2.035 (13); W–S(1), 2.527 (3); W–S(2), 2.544 (3); W–S(3), 2.496 (3); W–S(4), 2.543 (3); C(11)–O(1), 1.198 (14); C(11)–C(12), 1.43 (2); C(12)–C(13), 1.49 (2); C(13)–C(14), 1.35 (2) Å. C(12)–C-(11)–O(1), 138.9 (12)°.

The reaction between $[W(\equiv CPh)Br(CO)_2(pic)_2]$[12] (**1**) (pic = 4-picoline) and allyl bromide (10 equiv) for 2 h at 40 °C in CH_2Cl_2 leads to formation of [W(C(Ph)CHCHMe)$Br_2(CO)_2$(pic)] (**2**) as the only carbonyl-containing product (eq 1). Dark brown



(1)



(2)

crystals of **2** are isolated in 46% yield after chromatography (silica gel/CH_2Cl_2) and recrystallization from CH_2Cl_2/pentane.[14] The

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(12) **1**: ν_{CO} (CH_2Cl_2) 1987 (s), 1898 (s) cm^{-1}. The synthesis of **1** follows the procedure described for $[W(CPh)Br(CO)_2(pyr)_2]$.[13]

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molecular structure of **2** is shown in Figure 1.[15] It contains an unusual vinylcarbene ligand. The bond distance between tungsten and the carbene carbon C(9) is characteristic of a tungsten–carbon double bond;[11,16,20b,c] the distances between tungsten and the vinyl carbon atoms C(16) and C(17) are very long for an olefinic group coordinated to tungsten[17] and even long compared to typical bond distances in tungsten–allyl complexes.[18] The C(9)–C(16) distance is close to the value expected for a single bond between two sp^2 carbon centers (1.48 Å) and the C(16)–C(17) distance is very close to values found in free olefins (1.35 Å).[19] The C(Ph)-CHCHMe ligand may, therefore, be described as an η^3-vinylcarbene ligand with a very weakly coordinated vinyl group.[20]

The characteristics of the vinylcarbene ligand in the present complex are intermediate between those of rigorously η^1-bonded vinylcarbene ligands, which are found in coordinatively saturated metal complexes,[3] and those of more strongly η^3-bonded ligands, which are found in low-valent iron complexes of the type $[Fe(C_3R_4)(CO_3]$[9d,22] and which appropriately may be described as η^3-allylidene ligands. The difference in bonding clearly reflects better π-back-bonding of the electron-rich, low-valent iron center to the vinyl group. In more electropositive metal complex systems the transfer of electron density from the metal to the ligand proceeds even further, resulting in metallacyclobutenes as in titanocene cyclobutenes.[23]

Addition of 2 equiv of sodium diethyldithiocarbamate to a suspension of **2** in THF gives a red orange solution of a species with two infrared absorptions in the carbonyl region at 1931 and 1850 cm^{-1}. This initial product is formulated as the tungsten dicarbonyl complex $[W(C(Ph)CHCHMe)(S_2CNEt_2)_2(CO)_2]$ (**3**). Compound **3** is unstable; it is activated toward coupling of the vinylcarbene ligand with a carbonyl ligand and transforms into the vinylketene complex $[W(S_2CNEt_2)OCC(Ph)CHCHMe)(CO)]$ (**4**) (two diastereomers) within 1 h at 50 °C (eq 2).[24] Complex **4** is isolated in 90% yield after recrystallization from CH_2Cl_2/hexane.[25] The molecular structure of **4** is shown in Figure 2.[15] The vinylketene ligand is bonded to the metal center via four carbon atoms. The W–C distances and the respective C–C distances are comparable to values found in tungsten and molybdenum butadiene complexes,[26] with a somewhat shortened bond between tungsten and the ketene carbonyl carbon atom.

Carbonyl–vinylcarbene coupling in the present system occurs slowly only after addition of two strong, chelating donor ligands. In the related (η^3-allylidene)tricarbonyliron[9d,21] and dicyclopentadienyltitanacyclobutene systems[27] formation of vinylketene ligands occurs in the presence of carbon monoxide under atmospheric pressure. Good transfer of electron density from the metal center to the vinylcarbene moiety appears to be a crucial factor favoring the carbonyl–vinylcarbene coupling step.

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Supplementary Material Available: Tables of atomic coordinates, bond lengths, and bond angles for **2** and **4** (8 pages); tables of observed and calculated structure factors for **2** and **4** (33 pages). Ordering information is given on any current masthead page.

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(14) **2**: ^1H NMR ($CDCl_3$) δ 5.61 (m, C*H*Me), 5.29 (d, $^3J_{CH} = 11.67$ Hz, C*H*), 1,86 (d, $^3J_{CH} = 6.11$ Hz, CH_3); ^{13}C NMR (DC_2Cl_2) δ 240.4 (*C*Ph), 122.9, 91.3 (*C*H*C*HMe); IR ν_{CO} (CH_2Cl_2) 2025 (m), 1944 (s) cm^{-1}.

(15) Crystal data for **2** and **4**. **2**: $C_{18}H_{17}Br_2NO_2W$, FW = 623.1, monoclinic, $P2_1$, $a = 7.549$ (3) Å, $b = 12.64$ (5) Å, $c = 9.931$ (4) Å, $\beta = 90.65$ (3)°, $V = 948.2$ (6) $Å^3$, $Z = 2$, $\rho_{calcd} = 2.18$ g cm^{-3}, μ(Mo Kα) = 109.2 cm^{-1}, 1663 unique observed date, $3 \leq 2\theta \leq 50°$, $R = 0.036$, $R_w = 0.037$. **4**: $C_{22}H_{30}N_2O_2S_4W{\cdot}CH_2Cl_2$, FW = 751.6, monoclinic, $P2_1/n$, $a = 10.406$ (2) Å, $b = 12.929$ (2) Å, $c = 21.658$ (4) Å, $\beta = 94.30$ (2)°, $V = 2905.6$ (9) Å, $Z = 4$, $\rho_{calcd} = 1.72$ g cm^{-3}, μ(Mo Kα) = 46.9 cm^{-1}, 3806 unique observed data, $3 \leq 2\theta \leq 50°$, $R = 0.055$. All intensity measurements were made at low temperature (−93 ± 3°C), using graphite-monochromated MoKα radiation ($\lambda = 0.71069$ Å) and a variable rate, ω-scan technique. Empirical absorption corrections were applied based on the azimuthal scans of suitable reflections. Data with $[|F_o| \geq 3\sigma(F_o)]$ were considered observed. The structures were solved by conventional heavy atom methods and refined by blocked-cascade least squares. All calculations were performed by using the SHELXTL programs.

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(20) Related metal vinylcarbene entities are found in $[(W{=}C(CMe_3)CHCHCMe_3)(\eta^5\text{-}C_5H_5)Cl_3]$,[21a] $[(W{=}C(CF_3)C(CF_3)C(Me)C(Me))(S\text{-}i\text{-}Pr)(\eta^5\text{-}C_5H_5)(CF_3C_2CF_3)]$,[21b] $[(W{=}CPhCPhCPhCHPh)(O)(S_2CNEt_2)$,[21c] and $[(Ta{=}CPhCPhCMeNCMe_3)(\eta^5\text{-}C_5H_5)(CH_3)]$.[21d]

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(24) Vinylketene complexes of the same type as **4** have previously been obtained by reaction of $[W(S_2CNR_2)_2(CO)_3]$ with cyclopropenes.[10c]

(25) Major diastereomer: ^1H NMR (ppm, $CDCl_3$) δ 5.30(d, $^3J = 7.82$ Hz, C*H*), 2.87 (m, C*H*Me), 2.01 (d, $^3J = 6.34$ Hz, CH_3); ^{13}C NMR (ppm, $CDCl_3$) δ 234.9 (C=O), 204.7 (CO), 79.4 (*C*H), 68.9(*C*HMe), 56.1 (*C*Ph).

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Stereospecific Binding of *rac*-Iron(III) *N*,*N'*-Ethylenebis[(5-bromo-2-hydroxyphenyl)glycinate] to the Bilirubin Site on Human Serum Albumin

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Metal complexes that recognize specific sites on biological macromolecules have potential as drugs and molecular probes.[1-5] Our interest in paramagnetic chelates as liver-enhancing relaxation agents for NMR imaging has led us to study the interactions between chelates and relevant binding proteins.[6-11] In vivo, these

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