First α,β-unsaturated mononuclear bisylidene complex of tungsten: synthesis and structure

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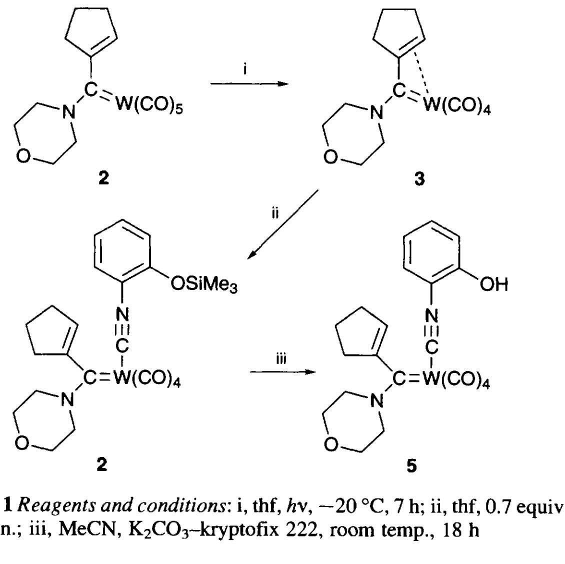
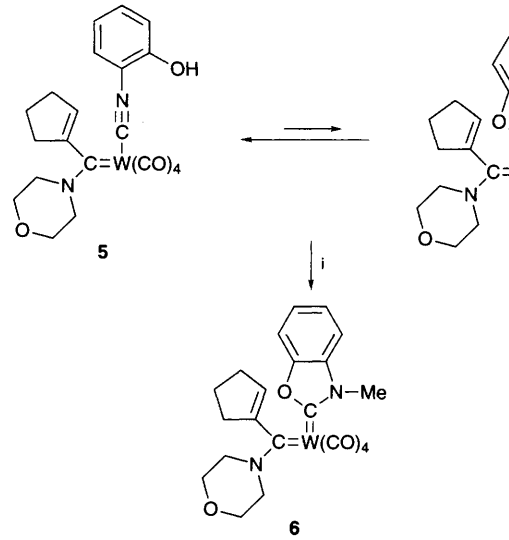
***cis*-Tetracarbonyl[(1-cyclopentenyl)(*N*-morpholino)methylidene](2-hydroxyphenyl isocyano)tungsten(0) 5 undergoes intramolecular cyclization by deprotonation and subsequent *N*-alkylation to give the novel bisylidene complex 6, which is characterized by a single-crystal X-ray structure analysis.**

Although great attention has been paid to investigations into Fischer ylidene complexes much less effort has been directed to complexes of the bisylidene Fischer type.[1] This may be due to the fact that bisylidene complexes, with a few exceptions,[2] cannot be prepared by direct reaction of carbonyl monoylidene transition-metal complexes with nucleophiles, such as alkyllithium reagents. Because of the strong electrophilic character of the ylidene centre the addition does not take place at one of the carbonyl ligands, but rather at the ylidene carbon. As an alternative, the photochemical exchange of CO in a pentacarbonyl ylidene complex for an appropriate ligand, which would behave as the precursor to the second ylidene function, could provide a new approach for the synthesis of bisylidene complexes. It was reported recently that 2-(trimethylsiloxy)phenyl isocyanide[3] **1** coordinated to a $M(CO)_5$ fragment (M = Cr, Mo, W) shows a strong tendency to cyclize upon desilylation to yield the corresponding ylidene complex.[4] We report here that compound **2** undergoes CO/isocyanide exchange and cyclization to give the bisylidene complex **6**.

A solution of pentacarbonyl ylidene complex **2**[6] in THF was irradiated at −20 °C for 7 h to afford the corresponding tetracarbonyl ylidene complex **3** (Scheme 1);‡ the loss of one carbonyl ligand was accompanied by a change in colour from yellow to red. Complex **3** was treated *in situ* with 0.7 equiv. of isocyanide **1** whereupon the colour changed immediately to yellow. After purification compound **4**§ was isolated in 62% yield. Desilylation of **4** was achieved with K_2CO_3–kryptofix 222 in acetonitrile leading exclusively to complex **5**.



Scheme 1 *Reagents and conditions*: i, thf, *hv*, −20 °C, 7 h; ii, thf, 0.7 equiv. **1**, 30 min.; iii, MeCN, K_2CO_3–kryptofix 222, room temp., 18 h



Scheme 2 *Reagents and conditions*: i, dmf, −40 °C, 1.15 equiv. $KOBu^t$, 3 h, then 1.5 equiv. MeI, room temp., 3 h

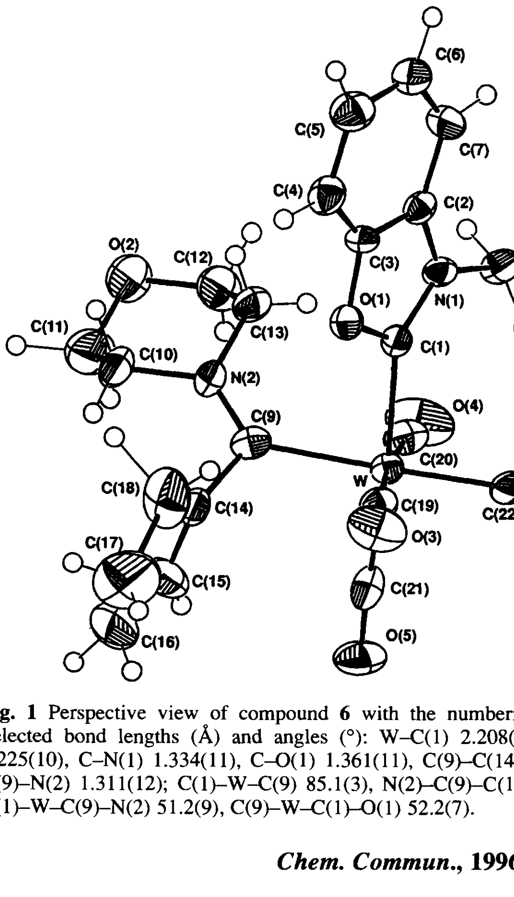


Fig. 1 Perspective view of compound **6** with the numbering scheme. Selected bond lengths (Å) and angles (°): W–C(1) 2.208(9), W–C(9) 2.225(10), C–N(1) 1.334(11), C–O(1) 1.361(11), C(9)–C(14) 1.500(13), C(9)–N(2) 1.311(12); C(1)–W–C(9) 85.1(3), N(2)–C(9)–C(14) 113.6(9), C(1)–W–C(9)–N(2) 51.2(9), C(9)–W–C(1)–O(1) 52.2(7).

The presence of the (amino)ylidene ligand in **5** leads to enhanced (d⟶p)π-back bonding from the metal centre to the isocyanide carbon. Because of this isocyanide deactivation of the latter intramolecular nucleophilic attack of the hydroxy group is not observed.[¶] The conversion of **5** into bisylidene complex **6**[§] was effected by deprotonation with KOBu^t in DMF at −40 °C and subsequent alkylation with MeI (Scheme 2); thus, the bisylidene **6** was obtained in an overall yield of 34% based on **2**. Crystallization of **6** from hexane–CH_2Cl_2 (1 : 1, *v*/*v*) at −20 °C provided air-stable yellow crystals (mp 157–158 °C). The X-ray crystal structure of **6** is shown in Fig. 1.[‖]

We were particularly interested in the preparation of an α,β-unsaturated bisylidene complex in order to investigate the influence of the second ylidene ligand upon reactions such as chromium-mediated benzannulation or [4 + 2] cycloaddition. Therefore, we also tried to prepare the chromium complex analogous to **6**, but we found that its precursor, **4-Cr**,[6] decomposed under the desilylation conditions. No decomposition products could be isolated after treatment with MeOH–KF or K_2CO_3–kryptofix 222–acetonitrile.[7]

Work to evaluate the potential of this method to produce polyylidene complexes starting from other pentacarbonyl ylidene complexes is in progress. Further attempts to prepare α,β-unsaturated bisylidene chromium complexes are also under way.

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Footnotes

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‡ All reactions and work-up procedures were performed with dry solvents and under a nitrogen atmosphere.

¶ The same observation was reported for a *cis*-tetracarbonyl(*N*- methyl-1,2-dihydrobenzoxazol-2-ylidene)(triphenylphosphino)tungsten(0); see ref. 5.

§ *Selected spectroscopic data*: **4**: IR (thf): $\nu_{C\equiv N}$ 2108m, ν_{CO} 1994s, 1921vs, 1907vs cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38–7.04 (m, 4H, H_{arene}), 5.34 (s, 1H, C = CH), 4.50–4.40 (br, 2H, OCH_2), 4.07 (t, $^3J_{HH}$ = 4.7 Hz, 2H, OCH_2), 3.95–3.85 (s, 4H, NCH_2), 2.61–2.49 (br, 3H), 2.10–1.89 (br, 3H), ($CH_2CH_2CH_2$), 0.49 [s, 9H, $Si(CH_3)_3$]; ^{13}C NMR (75 MHz, $CDCl_3$): δ 257.1 (ylidene C), 207.8 (*trans*-ylidene CO), 204.5 (*trans*-isocyanide CO), 200.8 (*cis*-CO), 163.4 (NC), 153.2 (C=CH), 151.2 (Ar–$COSiMe_3$), 129.0, 126.9, 121.7, 120.5 (C_{arene}), 119.2 (Ar–CNC), 120.4 (C=CH), 67.9, 67.8(OCH_2), 61.6, 53.0 (NCH_2), 35.5, 33.0, 23.4 ($CH_2CH_2CH_2$), 0.1 ($Si(CH_3)_3$).

6: IR (CH_2Cl_2): ν_{CO} 2002m, 1898s, 1872vs cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33–7.06 (m, 4H, H_{arene}), 4.87 (s, 1H, C=CH), 4.38–4.27 (br, 2H, OCH_2), 3.99 (s, 3H, NCH_3), 3.81 (t, $^3J_{HH}$ 4.7 Hz, 2H, OCH_2), 3.72–3.64 (br, 4H, NCH_2), 2.39–2.30 (br, 3H), 1.88–1.77 (br, 3H), ($CH_2CH_2CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 259.3 (NCC, ylidene), 223.1 (NCO, ylidene), 212.1 (*trans*-NCC-ylidene CO), 210.7 (*trans*-NCO-ylidene CO), 203.6 (CO *trans* CO), 153.5 (C=CH), 152.2 (Ar–CO), 131.8 (Ar–CN), 124.7, 124.5, 110.4, 110.1 (C_{arene}), 118.3 (C=CH), 67.9, 67.8 (OCH_2), 61.3, 52.8 (NCH_2), 35.5 (NCH_3), 34.9, 32.9, 23.3 ($CH_2CH_2CH_2$); HRMS: *m*/*z* 564.1004 (M^+ − CO), calc. 564.1004); EIMS: *m*/*z* 592 (M^+, 1.6), 564 (M^+ − CO, 38), 536 (M^+ − 2CO, 65), 480 (M^+ − 4 CO, 27), 165 (M^+ − ylide − $W(CO)_4$, 100%).

‖ *Crystal data* for **6**: $C_{22}H_{22}N_2O_6W$, M_r = 594.27, monoclinic, space group $P2_1/c$ determined from the systematic absences, a = 16.163(9), b = 8.346(2), c = 16.643(8) Å, β = 99.87(5)°, U = 2212(2) Å^3, Z = 4, D_c = 1.78 Mg m^{-3}, Mo-Kα radiation (graphite-crystal monochromator, λ = 0.710 73 Å), μ = 53.71 cm^{-1}, $F(000)$ = 1160, T = 200(2) K. The intensity data of 3577 reflections were measured. Some double measured reflections were averaged, $R_{int} = \Sigma(I - <I>)/\Sigma I = 0.081$, resulting in 3061 'unique' reflections. The structure was solved by the Patterson method using the program DIRDIF (Beurskens, 1992). An empirical absorption correction was applied using XABS2 (Parkin, Moezzi and Hope, 1995). All the hydrogen atoms were found by difference-Fourier synthesis using low-angle data. The hydrogen atoms were isotropically refined with a common thermal parameter. Final conventional R = 0.039 [for 2052 $F_o > 4\sigma(F_o)$], and $wR2$ = 0.113 (for a total of 3061 'unique' reflections), $wR2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0691P)^2\ 0.73P]$ where $P = [\max.(F_o^2,0) + 2{*}F_c^2]/3$. Goodness-of-fit on $|F|^2$ 1.051. Total number of parameters 347. All refinements were made using SHELXL93 (G. M. Sheldrick, 1993). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/253.

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