Benzoyl–Carbene Coupling by $[\mathrm{CpM(COPh)(CO)_2\{=\overline{C(CH_2)_3N}Me\}}]$ (M = Mo, W)

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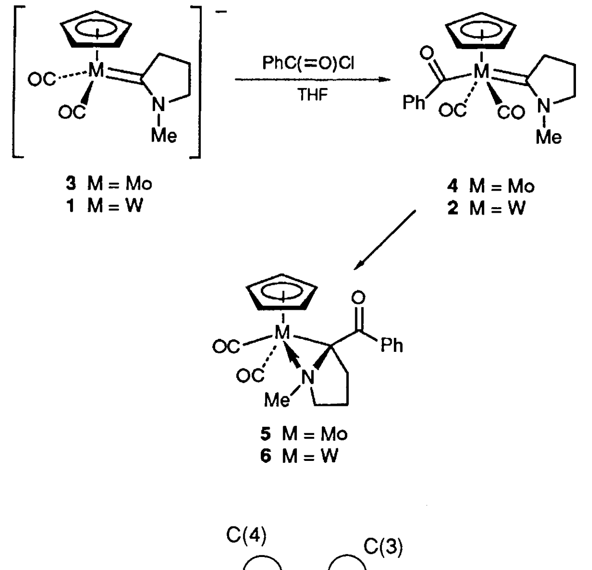
Treatment of the anions $[\mathrm{CpM\{=\overline{C(CH_2)_3N}Me\}(CO)_2}]$ (M = Mo or W) with PhC(=O)Cl results in the corresponding η¹-benzoyls $[\mathrm{CpM(\eta^1\text{-}COPh)\{=\overline{C(CH_2)_3N}Me\}(CO)_2}]$ which undergo benzoyl–carbene coupling, most likely through 1,2-migrations of benzoyl to carbene, in forming the complexes $[\mathrm{Cp\underline{M\{\eta^2\text{-}\overline{C(COPh)(CH_2)_3N}}Me\}(CO)_2}]$.

Migratory insertion to coordinated carbonyl is one of the most important fundamental processes within organotransition metal chemistry.[1] This process is relatively well understood. Migration to coordinated carbene is less well understood and less common, although some well defined migrations, particularly of hydride, are known.[1,2] This process is much less well understood than migratory insertion reactions of carbonyl principally because of the relative paucity of suitable (that is, isolable or spectroscopically identifiable) complexes [ML$_n$R(carbene)]. Formation of a C–C bond through migration of acyl groups to carbene in a mononuclear transition metal system appears to be an unknown process. We report such a process here. One or two examples of acyl–carbyne coupling reactions in bimetallic complexes are known.[3]



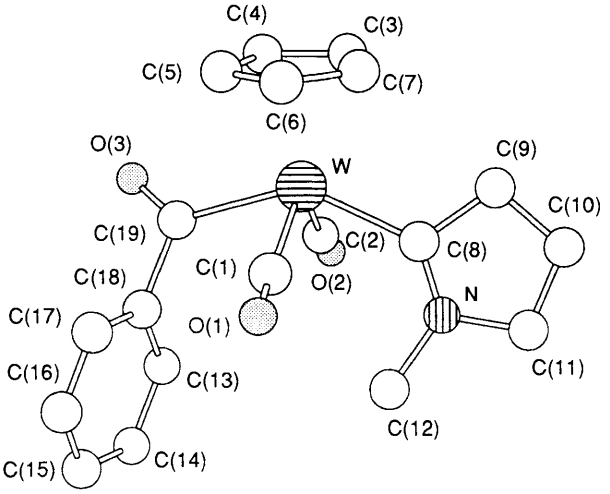


Fig. 1 The molecular structure of $[CpW(\eta^1\text{-}COPh)\{=C(CH_2)_3NMe\}(CO)_2]$ **2**. Important bond distances (Å) and angles (°): W–C(1) 1.897(25), W–C(2) 1.902(25), W–C(8) 2.128(21), W–C(19) 2.232(29), C(19)–O(3) 1.184(40), C(19)–C(18) 1.535(35); C(1)–W–C(8) 83.9(9), C(1)–W–C(2) 107.5(11), C(1)–W–C(19) 78.3(9), C(8)–W–C(2) 73.3(9), C(8)–W–C(19) 135.9(10), C(2)–W–C(19) 74.2(11), O(3)–C(19)–C(18)–C(17) −85.7.

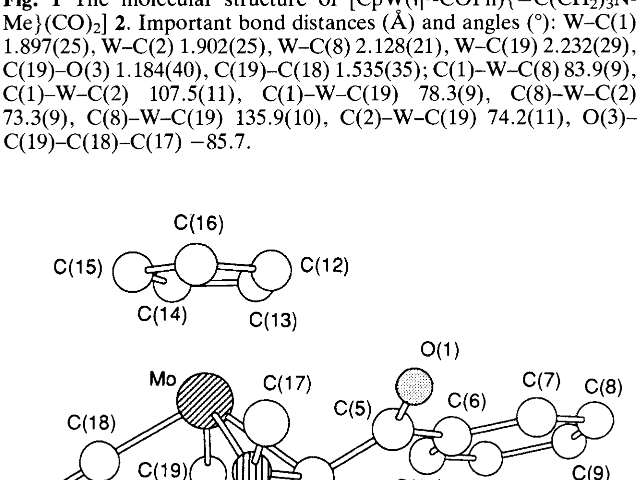


Fig. 2 The molecular structure of $[CpMo\{\eta^2\text{-}C(COPh)(CH_2)_3NMe\}(CO)_2$ **5**. Important bond distances (Å) and angles (°): Mo–N 2.211(8), Mo–C(1) 2.235(10), Mo–C(18) 1.941(8), Mo–C(19) 1.946(8), C(1)–N 1.464(9), C(1)–C(5) 1.486(11), C(5)–O(1) 1.226(9); C(1)–Mo–N 38.4(3), N–Mo–C(19) 108.6(4), N–Mo–C(18) 89.6(4), C(1)–Mo–C(19) 84.1(4), C(1)–Mo–C(18) 112.5(4), C(19)–Mo–C(18) 76.4(3), C(17)–N–C(1)–C(5) −4.7, O(1)–C(5)–C(6)–C(7) −20.2.

Addition of PhC(=O)Cl to solutions of the anion $[CpW\{=C(CH_2)_3NMe\}(CO)_2]^-$ **1**[4] in tetrahydrofuran (THF) results in displacement of chloride and formation of the isolable η^1-benzoyl $[CpW(\eta^1\text{-}COPh)\{=C(CH_2)_3NMe\}(CO)_2]$ **2** (52%).† The NMR spectra show this to exist as a mixture of *cis* and *trans* isomers, with the *trans* predominant. The IR spectrum has the characteristic appearance of a *trans* dicarbonyl with shoulders corresponding to the *cis* isomer. The solid state IR spectrum suggests only the *trans* isomer. The X-ray crystal structure is displayed in Fig. 1 and confirms that **2** has a *trans* structure in the solid state. The phenyl ring lies out of the plane of the acyl group, with a torsion angle of −85.7°, allowing no opportunity for conjugation.[5]

The reaction of $[CpMo\{=C(CH_2)_3NMe\}(CO)_2]^-$ **3** with PhC(=O)Cl proceeds in an analogous fashion. In this case the product $[CpMo(COPh)\{=C(CH_2)_3NMe\}(CO)_2]$ **4** is not isolable but the IR spectrum of the reaction mixture is closely comparable to that of the isolable **2**, suggesting the presence of **4** in solution. Complex **4** is not isolable since it isomerizes over a few minutes at ambient temperature to the new complex **5** (53%).‡ The X-ray crystal structure of **5** is displayed in Fig. 2.

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† $[CpW(\eta^1\text{-}COPh)\{=C(CH_2)_3NMe\}(CO)_2]$ **2**, yellow, m.p. 108–110 °C, decomp. Found: $[M + H]^+$, 494; C, 46.64; H 4.08; N 2.83%. $C_{19}H_{19}NO_3W$ requires $[M + H]^+$, 494; C, 46.25; H, 3.85; N, 2.84%. ^{1}H NMR ($CDCl_3$: ratio *cis* : *trans* = 2 : 3. *Cis* isomer δ 7.23, 7.08 (m, 5 H, Ph), 5.46 (s, 5 H, Cp), 3.76 (t, *J* 7.5 Hz, 2 H, $=CCH_2$), 3.25 (t, *J* 1 Hz), 3 H, NMe), 3.20 (q of t, *J* 1, 8 Hz, 2 H, CH_2NMe) and 1.87 (m, 2 H, central CH_2); *trans* isomer δ 7.23, 7.08 (m, 5 H, Ph), 5.44 (s, 5 H, Cp, 3.76 (t, *J* 7.5 Hz, 2 H, $=CCH_2$), 3.53 (t, *J* 1 Hz, 3 H, NMe), 3.02 (q of t, *J* 1, 7.5 Hz, 2 H, CH_2NMe) and 1.87 (m, 2 H, central CH_2). ^{13}C NMR ($CDCl_3$, −50 °C) *cis* isomer δ 264.2 (COPh), 243.5, 242.1, 242.0 (2 CO, W=C), 160.2 (*ipso*-Ph), 126.7 (Ph), 122.0 (Ph), 95.3 (Cp), 60.1 ($=CCH_2$), 55.1 (CH_2NMe), 43.0 (NMe) and 21.3 (central CH_2); *trans* isomer δ 262.2 (COPh, J_{WC} 63 Hz), 238.7 (W=C, J_{WC} 83 Hz), 230.4 (2 CO, J_{WC} 163 Hz), 160.4 (*ipso*-Ph), 127.5 (Ph), 127.3 (Ph), 121.1 (Ph), 94.5 (Cp), 60.7 ($=CCH_2$), 54.1 (CH_2NMe), 41.6 (NMe) and 21.3 (central CH_2).

Crystal data: monoclinic, a = 11.427(8), b = 14.296(15), c = 10.468(6) Å, β = 95.29(5)°, U = 1703(2) Å^3; D_c = 1.924 g cm^{-3}, Z = 4. Space group $P2_1/n$ [a non-standard setting of $P2_1/c$ (C^5_{2h}, No. 14), Mo-Kα radiation (λ = 0.71069 Å), μ(Mo-Kα) = 69.45 cm^{-1}, F(000) = 951.71. Data were collected in the range $3.5 < 2\theta < 50$ ° on a Nicolet R3 diffractometer by the ω-scan method. The structure was solved by conventional Patterson and Fourier techniques and refined by blocked cascade least squares methods to a final R 0.0872 (R_w 0.0671, 107 parameters) with allowance for the thermal anisotropy of tungsten and oxygen only using the 1647 independent reflections for which $|F|/\sigma(|F|) > 3.0$. A weighting scheme of $w = 1/(\sigma^2(F) + 0.00013(F^2)$ was used in the latter stages of refinement. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ $[CpMo\{\eta^2\text{-}C(COPh)(CH_2)_3NMe\}(CO)_2$ **5**, orange, m.p. 121–123 °C. Found: $[M]^+$, 407; C, 56.37; H, 4.83; N, 3.46%. $C_{19}H_{19}{}^{98}MoNO_3$ requires $[M]^+$, 407; C, 56.30; H, 4.69; N, 3.46%. IR ν_{CO}/cm^{-1} 1942s, 1831s and 1632m. ^{1}H NMR ($CDCl_3$) δ 8.11 (m, 2 H, Ph), 7.46 (m, 3 H, Ph), 5.22 (s, 5 H, Cp), 3.43 (s, 3 H, NMe), 3.35 (d of d of d, *J* 3, 5.5 and 10 Hz, 1 H, CH_2NMe), 3.03 (q, *J* 10 Hz, 1 H, CH_2NMe), 2.72 [d of d of d, *J* 3, 5 and 13 Hz, 1 H, CH_2(COPh)], 2.30 [t of d, *J* 9.5 and 13 Hz, 1 H, CH_2(COPh)] and 1.47 (m, 2 H, central CH_2). ^{13}C NMR ($CDCl_3$, −50 °C) δ 253.8 (CO), 248.7 (CO), 202.0 (COPh), 139.7 (*ipso*-Ph), 131.7 (Ph), 128.9 (Ph), 128.1 (Ph), 95.9 (Cp), 66.6, 64.5 [Mo–C(COPh), CH_2NMe], 54.8 (NMe), 34.4 [CH_2C(COPh)] and 19.9 (central CH_2).

Crystal data: triclinic, a = 8.117(12), b = 8.796(11), c = 13.029(16) Å, α = 74.46(9), β = 74.41(10), γ = 77.63(10)°, U = 853.1(18) Å^3; D_c = 1.578 g cm^{-3}, Z = 2. Space group $P\bar{1}$ (C^1_i, No. 2), Mo-Kα radiation (λ = 0.71069 Å), μ(Mo-Kα) = 7.65 cm^{-1}, F(000) = 411.87. The data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 diffractometer by the ω-scan method. The structure was solved by conventional Patterson and Fourier techniques and refined by blocked cascade least-squares methods to a final R 0.0558 with allowance for the thermal anisotropy of all ordered non-hydrogen atoms using the 2322 independent reflections for which $|F|/\sigma(|F|) > 3.0$.

The benzoyl and NMe groups are both *syn* to the cyclopentadienyl ring. The reaction forming **5** is stereospecific. Complex **5** possesses three chiral centres; hence there are potentially eight stereoisomers. However, the ^{1}H and ^{13}C NMR spectra of **5** displays only one set of signals suggesting the presence of just one enantiomeric pair.

Complex **2** isomerizes in analogous fashion to form **6** (16%), but requires more severe conditions (brief heating at reflux in THF). The spectroscopic properties of **6** are comparable to those of **5**, but the IR and NMR spectra now show two isomers in the ratio 4 : 1.

The simplest interpretation for the isomerizations of **2** to **6** and **4** to **5** is that the benzoyl undergoes a 1,2 migratory shift to the carbene atom, probably from the *cis* isomers rather than from the *trans* isomer.

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