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Reactivity of α-Metallated Alkylarene Tricarbonylchromium Complexes. Preparation, Properties and X-Ray Crystal Structure of $(\eta^3\text{-}C_3H_5)Pd(CH_2Ph\text{-}\eta^6)\text{–}Cr(CO)_3$, a Novel Complex with a Palladium–Chromium σ-Bond

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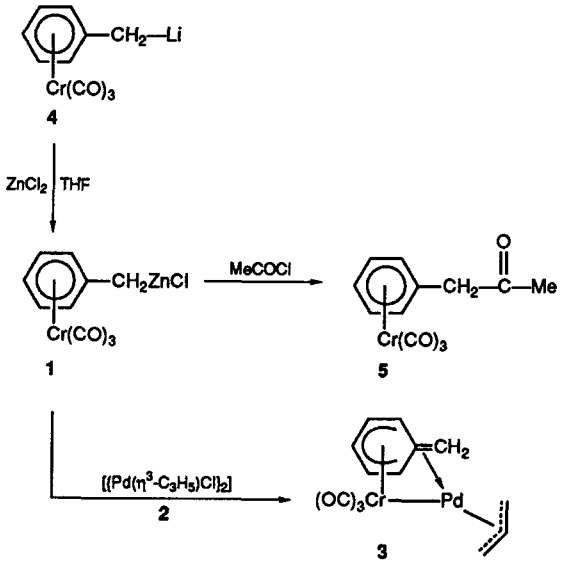
The reaction of $[Cr(\eta^6\text{-}PhCH_2ZnCl)(CO)_3]$ **1** with $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ **2** in tetrahydrofuran yields a novel complex $[(\eta^3\text{-}C_3H_5)Pd(CH_2Ph\text{-}\eta^6)\text{–}Cr(CO)_3]$ **3** with a Pd–Cr bond; the reaction of **3** with PhI leads to $[Cr(CO)_3(\eta^6\text{-}PhCH_2Ph)]$.

Recently we have reported[1] a simple method for the selective metallation of alkylarene tricarbonylchromium complexes in the benzyl position by use of lithium amides. This method allows various α-lithiated alkylarene tricarbonylchromium complexes to be prepared which are of synthetic interest in introducing the possibility of benzyl functionalization of an arene ligand.

In the present work we have found that the lithiated complex **4**, on treatment with $ZnCl_2$ in tetrahydrofuran (THF), readily forms the organozinc derivative **1** (Scheme 1). Whereas complex **4** reacts with MeCOCl (THF, − 78 °C, 10 min) yielding a complex mixture of products, the reaction of **1** with MeCOCl (THF, 20 °C, 1.5 h) produces the ketone **5** in 50% yield.

The reaction of **1** with allylpalladium chloride **2** unexpectedly yielded (in 50% yield) the novel palladium-containing



Scheme 1

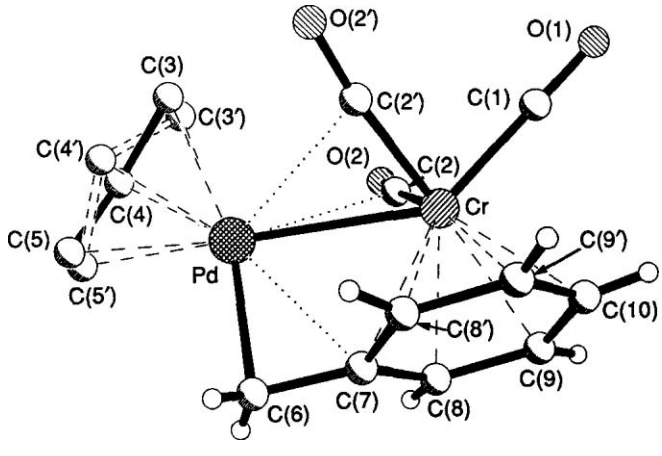
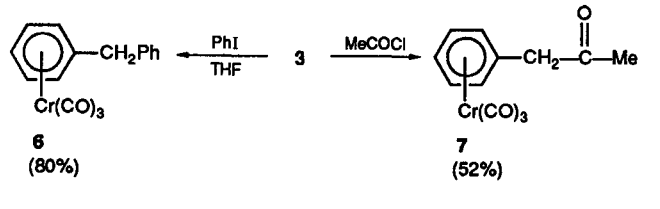


Fig. 1 Molecular structure of **3**. Both positions of the disordered allyl ligand are shown; primed atoms are symmetry related by a mirror plane. Selected bond distances (Å) and angles (°): Pd···C(2) 2.639(5), Pd–C(3) 2.25(1), Pd–C(4) 2.13(1), Pd–C(5) 2.16(1), Pd–C(6) 2.10(1), Pd–C(7) 2.53(1), Cr–C(1) 1.844(8), Cr–C(2) 1.857(6), Cr–C(7) 2.303(8), Cr–C(8) 2.228(6), Cr–C(9) 2.231(6), Cr–C(10) 2.21(1), C(3)–C(4) 1.40(2), C(4)–C(5) 1.45(3), C(6)–C(7) 1.42(1), C(7)–C(8) 1.433(7), C(8)–C(9) 1.394(7), C(9)–C(10) 1.397(7), Cr–η^6-ring plane 1.74; Pd–C(6)–C(7) 89.6(7), Cr–C(2)–O(2) 172.9(4).



Scheme 2

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complex **3**, whose structure was elucidated by a single crystal X-ray diffraction study.†

Molecules of **3** (Fig. 1) lie on a mirror plane passing through Pd, Cr, C(1), C(6), C(7) and C(10) and bisecting (dihedral angle 65°) the η^3-allyl ligand, which is thus disordered over two positions. The metal atoms are linked by a direct Pd–Cr bond [2.764(1) Å], two semibridging CO groups and an η^6:σ-bridging benzyl ligand; the coordination of the benzyl ligand with the Pd atom may, however, also be considered to be strongly asymmetric η^2 to the C(6) and C(7) atoms.

Complex **3**, which can be purified by chromatography on Al_2O_3, is an orange crystalline substance, moderately air-stable (for several hours at room temperature) and decomposing on heating at 118 °C. It is readily soluble in ether, benzene, chloroform and THF, decomposing in solution much faster than in the solid state. On heating in refluxing THF with PhI or MeCOCl, complex **3** forms the corresponding derivatives **6** and **7**.

† *Crystal data* for **3**: $C_{13}H_{12}CrO_3Pd$, $M = 374.6$, monoclinic, space group $P2_1/m$, $a = 7.200(2)$, $b = 9.243(2)$, $c = 10.064(2)$ Å, $\beta = 106.22(2)°$, $V = 643.1(2)$ Å^3, $Z = 2$, $D_c = 1.93$ g cm^{-3}. The X-ray diffraction experiment was carried out with a Siemens P3/PC diffractometer ($T = 193$ K, graphite-monochromated Mo-Kα radiation, $\lambda = 0.71069$ Å, θ–2θ scan technique, $2\theta \leq 50°$, 934 observed independent reflections with $I > 2\sigma(I)$). The structure was solved by the Patterson method, using SHELXTL PLUS programs. Least-squares refinement, anisotropic for non-hydrogen atoms and isotropic for hydrogens located from a difference Fourier synthesis (with the exception of the disordered allylic atoms), converged at $R = 0.033$ and $R_w = 0.041$. Atomic coordinates, thermal parameters, and bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *J. Chem. Soc., Chem. Commun.*, 1991, Issue 1.

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Reference

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