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Preliminary Communication

Synthesis of a bridging-imido η-cycloheptatrienyl molybdenum complex

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Abstract

Treatment of $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}Cl)_3Mo(\eta\text{-}C_7H_7)]$ (**1**) with ArNHLi (Ar = 2,6-diisopropylphenyl) gives the bridging-imido binuclear compound $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}NAr)_2Mo(\eta\text{-}C_7H_7)]$ (**2**), which is the first example of a transition-metal imido compound with a η-cycloheptatrienyl ligand.

Transition metal imido complexes are of much current interest not only because of their industrial [1] and biological [2] relevance but also because of their involvement in alkene metathesis [3] and carbon–hydrogen bond activation [4]. Although many organometallic imido complexes with a variety of co-ligands have been reported, those with the η-cycloheptatrienyl group as supporting ligand are unknown. As part of our systematic study of the cycloheptatrienyl-transition metal chemistry [5–7], we describe here the preparation of the first transition-metal imido complex with η-cycloheptatrienyl ligand, namely $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}NAr)_2 Mo(\eta\text{-}C_7H_7)]$ (Ar = 2,6-diisopropylphenyl) (**2**).

The previously described dimer $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}Cl)_3Mo(\eta\text{-}C_7H_7)]$ (**1**) [8] was treated with $^tBuNHSiMe_3$, but no reaction was observed even upon prolonged heating. Treatment of **1** with 3 equivalents of ^tBuNHLi in tetrahydrofuran (THF) gave an intractable brown material. However, the reaction between **1** and 3 equivalents of ArNHLi (Ar = 2,6-diisopropylphenyl) in THF yielded a brown suspension from which dark red crystals of $[(\eta\text{-}C_7H_7)Mo(\mu\text{-}NAr)_2Mo(\eta\text{-}C_7H_7)]$ (**2**) were isolated in 56% yield.

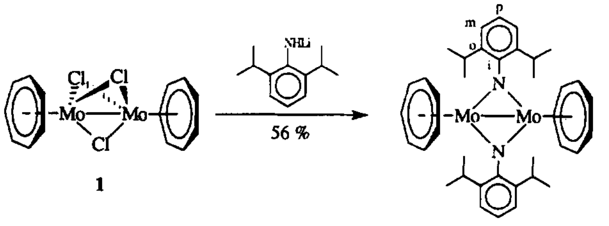
The analytical and spectroscopic data allowing characterisation of the compound **2** are given in the Experimental section. The compound **2** is very air-sensitive both in solid state and in solution. Nevertheless, satisfactory microanalysis was obtained. The fast atom bombardment (FAB) mass spectrum of **2** did not show a parent M^+ peak, but it gave peaks centred at m/z 362 as the base peak which is assignable to the fragment $[Mo(\eta\text{-}C_7H_7)(NAr)]^+$. The isotope pattern of these peaks was in good agreement with that obtained from simulation. The ^1H NMR spectrum of **2** in C_6D_6 showed a doublet at δ 7.24 and a triplet at δ 7.12 assignable to the phenyl protons H_m and H_p, respectively; a sharp singlet at δ 4.55 may be assigned to the $\eta\text{-}C_7H_7$ protons, and a septet at δ 2.77 and a doublet at δ 1.19 to the isopropyl groups. The ^{13}C NMR spectrum supported the ^1H NMR assignments. The sharp bands observed in the NMR spectra indicate that **2** is diamagnetic. Therefore we propose for **2** the structure shown in Scheme 1.

There is substantial evidence that the $\eta\text{-}C_7H_7$ ligand requires three electrons from the metal centre in the formation of the metal-ligand bond [5a,6b]. Since the imido ligand is a four electron donor and a metal-metal bond is involved, both metals achieve an 18 electron count.

Preliminary studies on the reactivity of the bridging-imido compound **2** showed that it remained intact upon treatment with PMe_3 or PPh_3.

1. Experimental details

The general techniques and equipment used are as described in ref. 7e. Compounds 2,6-diisopropylaniline and butyllithium were used as received (Aldrich) and compound **1** was prepared as described [8].



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Scheme 1.

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1.1. *Preparation of [(η-C_7H_7)Mo(μ-NAr)$_2$Mo(η-C_7H_7)] (Ar = 2,6-diisopropylphenyl) (2)*

To a solution of 2,6-diisopropylaniline (0.75 cm^3, 4.0 mmol) in THF (10 cm^3) was added butyllithium (1.6 mol dm^{-3} solution in hexane, 2.5 cm^3, 4.0 mmol), giving a very pale yellow solution. This was transferred to a stirred suspension of [(η-C_7H_7)Mo(μ-Cl)$_3$Mo(η-C_7H_7)] (1) (0.5 g, 1.3 mmol) in THF (30 cm^3) pre-cooled to −78°C. The mixture was allowed to warm to room temperature during 3 h then stirred overnight, forming a dark brown suspension. The volatiles were removed *in vacuo* and the residue was extracted with pentane (3 × 30 cm^3). The extract was filtered and the filtrate was kept at −80°C overnight. A small amount of a precipitate separated and was filtered off. The filtrate was concentrated to *ca.* 40 cm^3 then cooled to −20°C to yield dark red crystals. These were filtered off and dried *in vacuo*. The filtrate was further concentrated and cooled again to give a second crop of product (0.26 g). The combined yield was 56%. Anal. Found: C, 61.13; H, 6.70; N, 3.88. $C_{38}H_{48}Mo_2N_2$ calc.: C, 62.98; H, 6.68; N, 3.87%. FAB MS (*m/z*): 362, [Mo(η-C_7H_7)(NAr)]$^+$ (based on ^{96}Mo). ^{1}H-NMR (C_6D_6): δ 7.24 [d, *J*(H–H) 7.5 Hz, H_m, 4 H], 7.12 [t, *J*(H–H) 7.5 Hz, H_p, 2 H], 4.55 (s, 14 H, η-C_7H_7), 2.77 [septet, *J*(H–H) 6.8 Hz, 4 H, C*H*Me_2], 1.19 [d, *J*(H–H) 6.8 Hz, 24 H, Me]. ^{13}C{^{1}H}-NMR (C_6D_6): δ 160.0 (C_i), 140.4 (C_o), 124.2 (C_m), 123.1 (C_p), 88.8 (η-C_7H_7), 26.7 (*C*HMe_2), 26.2 (Me). IR (KBr): 3044w, 2962s, 2923m, 2865m, 1462m, 1420s, 1380m, 1360m, 1313s, 1243s, 1205m, 1099m, 1050w, 966m, 929m, 906m, 857m, 813m, 800m, 783vs, 762vs, 711w, 524w.

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