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**Preliminary communication**

**Unexpected regioselectivity in the addition of lithium diisopropylamide to ( $\eta^4$ -1,3-butadiene)Co(CO)<sub>3</sub>BF<sub>4</sub>**

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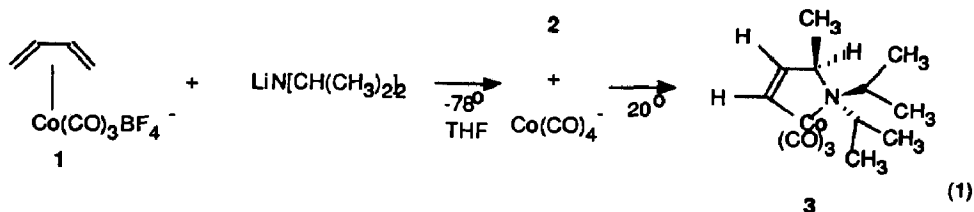
**Abstract**

The reaction of LiN[CH(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> with ( $\eta^4$ -1,3-butadiene)Co(CO)<sub>3</sub>BF<sub>4</sub> (**1**) produces a novel metallacycle HC=CHCH(CH<sub>3</sub>)N[CH(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Co(CO)<sub>3</sub> (**3**) which apparently arises via initial addition of the nucleophile at C(2) of the coordinated diene.

There has been considerable recent interest in the chemistry of nucleophilic additions to metal-diene complexes, especially of Fe [1], Mo [2], Pd [3] and Co [4], both in terms of mechanistic aspects and synthetic applications. In all the examples reported to date nucleophiles have been found to add specifically to the internal carbon (C(2)) in the iron [Fe(CO)<sub>3</sub>] system (under kinetic control) but to the terminal carbon (C(1)) in the Mo[CpMo(CO)<sub>2</sub>]<sup>+</sup>, Pd[PdX<sub>2</sub>] and Co[Co(CO)<sub>3</sub>]<sup>+</sup> complexes. The factors controlling the regiochemical course of these reactions including the metal, charge, auxiliary ligands and the nucleophile have been analyzed theoretically [5]. In this report we provide evidence for the first example of C(2) nucleophilic attack involving the ( $\eta^4$ -diene)Co(CO)<sub>3</sub>BF<sub>4</sub> compounds (**1**) which illustrates the powerful effect of the nature of the nucleophile on the regioselectivity of such reactions].

Treatment of a yellow THF suspension of **1** with 1.0 equiv. of LiN[CH(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (from BuLi/NH[CH(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>) in THF/HMPA (3 : 1) at –78 °C rapidly produced an orange-red solution which exhibited IR bands due to LiCo(CO)<sub>4</sub> (1880 cm<sup>-1</sup>) and a new species **2** (2060(m), 1980(s) cm<sup>-1</sup>). Upon warming to 20 °C **2** was transformed over several hours to a new product **3** (2020(m), 1940(2) cm<sup>-1</sup>) which could be isolated (35–45% yield) as a moderately stable orange oil following chromatography on silica gel (eq. 1).

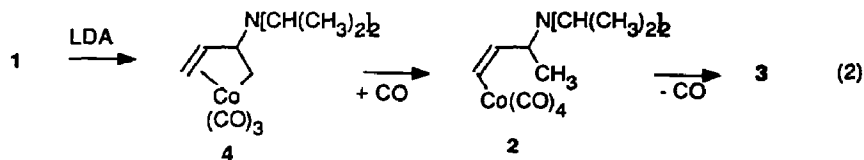
\* Reference numbers with asterisks indicate notes in the list of references.



Product **3** was assigned the unexpected metallacycle structure above based on the following key data. Its  $^1\text{H}$  NMR spectrum (300 MHz,  $\text{C}_6\text{D}_6$ ) consisted of a distinctive pattern for the two vinylic protons at 6.13 (d,  $J$  11 Hz) and 3.79 (dd,  $J$  11, 8 Hz) [6\*] and the C(3) methine proton at 3.51(m) which is also coupled with the C(4) methyl resonance at 1.20 (d,  $J$  7 Hz). The inequivalent isopropyl-methine resonances at 2.78(m) and 3.41(m) and the appearance of four isopropyl-methyl resonances (0.92, 0.78, 0.67, 0.63; d,  $J$  7 Hz) indicate quaternarization of the N and the presence of the adjacent asymmetric center. These assignments were supported by homonuclear decoupling and  $^{13}\text{C}$  NMR spectral data [7\*]. The IR spectrum of **3** suggested an electron rich  $\text{Co}(\text{CO})_3$  unit [8\*] while its mass spectrum (12 eV; 297 (16,  $M^+$ ), 269 (97,  $M^+ - \text{CO}$ ), 241 (83,  $M^+ - 2\text{CO}$ ), 213 (84,  $M^+ - 3\text{CO}$ ), 154 (100,  $M^+ - \text{Co}(\text{CO})_3$ ) indicated the composition  $\text{C}_{13}\text{H}_{20}\text{CoNO}_3$ .

Aside from the novelty of the heterocyclic unit of **3** [9\*], the atomic connectivity found establishes clearly that the nucleophilic attack by  $\text{N}(\text{Pr}^i)_2^-$  occurs at C(2) of the coordinated diene, the first such example involving a cationic diene complex. This result violates the Davies–Green–Mingos “rules” relating to the regiochemistry of nucleophilic attack on cationic  $\pi$ -complexes [5a] and illustrates the regiodependency of such reactions on the nucleophile’s electronic character. The nucleophile  $\text{N}(\text{Pr}^i)_2^-$  is the hardest and (next to  $\text{PhMgBr}$ ) the most basic of those which have been coupled with **1** (cf.  $\text{R}_3\text{N}$ ,  $\text{R}_3\text{P}$ ,  $\text{RO}^-$ ,  $\text{BH}_3\text{CN}^-$ , enol silanes and stabilized enolates), a feature which may explain its unique behavior [5b].

The mechanism by which **3** is formed from the initial adduct (viz. **4**) is presently unknown but it would appear to require an unusual vinylic C–H activation and H-transfer sequence. Some clues may lie in the identity of intermediate **2**. Efforts to characterize **2**, however, have been hampered by its facile conversion to **3** but the fact that its lifetime is greatly extended under an atmosphere of CO, the similarity of its NMR spectrum [10\*] to that of **3**, and its higher energy  $\nu(\text{CO})$ 's relative to **3** leads us to suspect a non-chelated structure (e.g. below) for **2**.



Additional studies of the mechanism of these reactions and the factors controlling the regiochemistry of nucleophilic additions to  $(\eta^4\text{-}1,3\text{-diene})\text{Co}(\text{CO})_3\text{BF}_4$  are in progress.

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## References and Notes

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- 6 Similarly separated  $\alpha$ - and  $\beta$ -vinyl proton resonances and  $J(\text{H-H})(\text{cis})$  are also seen in some acyclic Re- and Co-vinyl complexes: G.S. Bodner, D.E. Smith, W.G. Hatton, P.C. Heah, S. Georgiou, A.L. Rheingold, S.J. Geib, J.P. Hutchinson, J.A. Gladysz, *J. Am. Chem. Soc.* 109 (1987) 7688; M.D. Johnson, B.S. Meeks, *J. Chem. Soc. B*, (1971) 185.
- 7  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ) 125.4, 56.4, 53.5, 49.0, 47.2, 23.8, 21.1, 20.9, 20.7, 19.2 (a vinylic resonance is probably obscured by the solvent peak).
- 8 Less electron rich  $\text{LCo}(\text{CO})_3$ , e.g. ( $\eta^3$ -allyl) $\text{Co}(\text{CO})_3$ , exhibit  $\nu(\text{CO})$  at ca. 2060 and 2000  $\text{cm}^{-1}$  (see e.g. ref. 4).
- 9 A brief survey of the literature netted no other examples of the metallodihydropyrrole system found in 3.
- 10  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ) of 2 (contaminated with 3 and organic impurities):  $\delta$  5.43 (d, 1H,  $J$  11 Hz), 3.73 (dd, 1H,  $J$  11.9 Hz), 3.42 (m, 2H), 2.58 (m, 1H), 0.77 (d, 6H,  $J$  6 Hz), 0.60 (d, 6H,  $J$  6 Hz). Connectivities and some coupling constants were determined by homonuclear decoupling experiments.