Journal of Organometallic Chemistry, 135 (1977) C6—C9
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

A NEW CHELATED *C,N*-BENZYLLITHIUM REAGENT AND SOME ORGANOMETALLIC DERIVATIVES OF SELECTED EARLY TRANSITION METALS

LEO E. MANZER

Central Research & Development Department, E.I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898 (U.S.A.)*

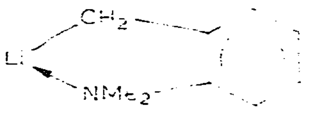
(Received March 23rd 1977)

Summary

The reactions of $LiCH_2C_6H_4$-*o*-NMe_2 with Cp_2MCl (M = Ti, V; Cp = η^5-C_5H_5), $CpTiCl_2$, $CrCl_3$, and $ScCl_3$ have led to the isolation of thermally stable, air-sensitive organometallic complexes whose stability is attributed to chelation. The reaction of $Cr(CH_2C_6H_4$-*o*-$NMe_2)_3$ with CO_2 gives a paramagnetic complex in which CO_2 has inserted into only one Cr—C bond and with diketones to give (diketonate)$Cr(CH_2C_6H_4$-*o*-$NMe_2)_2$.

Organometallic complexes of the early transition metals are generally quite reactive and unstable [1,2]. However, the use of bulky alkyl substituents [1—4] such as CH_2SiMe_3 and $CH(SiMe_3)_2$ have yielded some very stable and interesting compounds. Recent work in our laboratory [5] as well as in others [6, 7] has shown that considerable stabilization of organometallic complexes of the early transition metals can be achieved by the use of chelated organic ligands. Therefore, we were interested in preparing an alkyl ligand with a "built-in" chelating group in the hopes of stabilizing early transition metal organic derivatives. In this communication we describe the preparation of such a ligand and some of its early transition metal derivatives.

n-Butyllithium reacts cleanly with a molar equivalent of *N,N*-dimethyl-*o*-toluidine in a hexane/ether solution (95/5) at 50°C to give a pale yellow, ether-free precipitate of I. It may be separated by filtration, washed with



(I)

---

[*] Contribution No. 2436.

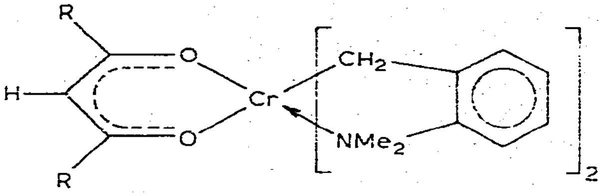
pentane, dried and stored indefinitely under an atmosphere of dry nitrogen. The integrated peak areas in the NMR spectrum of I in deuterated tetrahydrofuran and deuterolysis which gave only $CH_2DC_6H_4$-*o*-NMe_2 are consistent with the structure indicated. Care should be exercised when handling I since it is pyrophoric in air. Jones and Hauser [8] have reported a similar α-lithiation reaction of *o*-methyldimethylbenzylamine.

The addition of $LiCH_2C_6H_4$-*o*-NMe_2 to a magnetically stirred suspension of Cp_2TiCl [9] in ether, under a nitrogen atmosphere, gave a dark green solution from which $Cp_2Ti(CH_2C_6H_4$-*o*-$NMe_2)$ (II) was isolated as a dark green, very air-sensitive, crystalline solid. The magnetic moment, determined in benzene, was 1.7 BM. Deuterolysis of II gave *o*-$Me_2NC_6H_4CH_2D$. Similarly, $Cp_2V(CH_2C_6H_4$-*o*-$NMe_2)$ was obtained as a very air-sensitive, green-brown crystalline solid from the reaction of I with Cp_2VCl [9] in ether. In contrast to $Cp_2TiCH_2C_6H_5$ [10] which decomposes at room temperature, II may be stored at room temperature for several days under nitrogen with no apparent decomposition. The vanadium complex is much less stable than the titanium complex and decomposes after several days at room temperature under a nitrogen atmosphere. The ESR spectrum of $Cp_2Ti(CH_2C_6H_4$-*o*-$NMe_2)$ is unusual in that it shows a doublet at $g = 1.981$ due to coupling of the electron with one hydrogen atom ($\langle a_H \rangle = 5.1$ G). The reason for the nonequivalence of the CH_2 hydrogens is not clear but it may be due to steric interactions [11].

Green and Lucas [12] tried to prepare, without success, monocyclopentadienyl compounds of the type $CpTiR_2$ by the reaction of $[CpTiCl_2]_x$ [13] with the lithium or Grignard reagent of R. They found that disproportionation occurred to give titanium(II) and titanium(V) compounds. In contrast, two equivalents of I reacted smoothly with $[CpTiCl_2]_x$ in ether to give $CpTi(CH_2C_6H_4$-*o*-$NMe_2)_2$ as a dark green, crystalline, very air-sensitive compound. The magnetic moment of 1.6 BM, which was determined in benzene by the Evans method [14], is consistent with a d^1-electronic configuration.

The reaction of $CrCl_3$ and $ScCl_3$ with three equivalents of II in tetrahydrofuran gave $M(CH_2C_6H_4NMe_2)_3$ as pyrophoric, red and pale-yellow crystalline solids, respectively. The chromium compound was recrystallized from dichloromethane without decomposition, while the scandium complex reacted violently with dichloromethane. The magnetic moment of $Cr(CH_2C_6H_4$-*o*-$NMe_2)_3$ was determined in CH_2Cl_2 and was found to be 3.6 BM. The organoscandium complex was diamagnetic and its NMR spectrum at room temperature in benzene-d_6 showed equivalent N—Me groups at δ 2.27 ppm and a singlet for the benzylic hydrogens at δ 1.64 ppm. The remarkable stability achieved by chelation of the organic ligand is illustrated by the fact that $Cr(CH_2C_6H_5)_3$ has not been isolated [15] and decomposes above −78°C; in contrast, $Cr(CH_2C_6H_4NMe_2)_3$ is thermally stable under nitrogen and melts cleanly at 168°C.

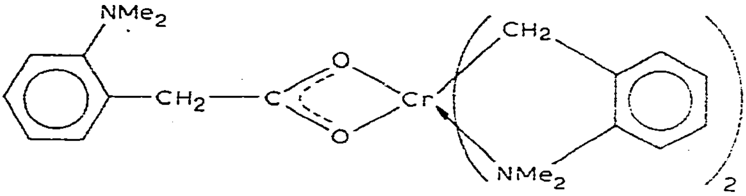
The addition of one equivalent of a 1,3-diketone to a suspension of $Cr(CH_2C_6H_4$-*o*-$NMe_2)_3$ in CH_2Cl_2 gave a very dark red-purple solution from which the new organochromium(III) compounds III were isolated in quantitative yields as crystalline solids with magnetic moments in the range 3.9—4.1 BM. The electronic spectrum of IIIa (R = t-Bu) showed a band in the visible



(IIIa) R = t-Bu
(IIIb) R = Me
(IIIc) R = Ph

region at 546 nm with a shoulder at 681 nm; the spectra of IIIb and IIIc showed single bands at 512 and 543 nm, respectively.

The reaction between $Cr(CH_2C_6H_4\text{-}o\text{-}NMe_2)_3$ and CO_2 at 15 psig in benzene was very slow at room temperature but at 75°C a rapid reaction took place to give a cherry red solution. From this solution was isolated a dark red, ether-soluble complex. The analytical data indicated that one CO_2 had been incorporated into the molecule. The magnetic moment (4.0 BM) and electronic spectrum (single band at 621 nm) were similar to III. The infrared spectrum did not show any strong bands in the 1675—1800 cm^{-1} region so structure IV is proposed.



(IV)

The isoelectronic chelated aryllithium reagent, $LiC_6H_4\text{-}o\text{-}CH_2NMe_2$, has been used extensively in recent years to prepare a number of arylmetal compounds of cobalt [16], gold [17], silver [18], nickel [19], palladium [19], platinum [19] and copper [20]. We have now extended this series of compounds to include aryl derivatives analogous to the benzyl derivatives described in this paper. The two series of compounds offer a unique opportunity to compare the chemistry and reactivity of metal—aryl and metal—alkyl bonds. Full details of the preparations and reactions of both aryl and alkyl compounds will be described at a later date.

All compounds described in this paper have been fully characterized by elemental and spectral analysis.

References

1 R.R. Schrock and G.W. Parshall, Chem. Rev., 76 (1976) 243.
2 P.J. Davidson, M.F. Lappert and R. Pierce, Chem. Rev., 76 (1976) 219.

3 W. Moffat, A. Shortland, G. Yagupsky, N.J. Hill, M. Yagupsky and G. Wilkinson, J. Chem. Soc. Dalton Trans., (1972) 533.
4 M.R. Collier, M.F. Lappert and R. Pierce, J. Chem. Soc. Dalton Trans., (1973) 445.
5a L.E. Manzer, R.C. Gearhardt, L.J. Guggenberger and J.F. Whitney, J. Chem. Soc. Chem. Commun., (1976) 942.
5b L.E. Manzer, J. Amer. Chem. Soc., 99 (1977) 276.
6 H.J. de Liefde Meijer and F. Jellinek, Inorg. Chem. Acta, 4 (1970) 651.
7 D. Ytsma, J.G. Hartswiker and J.H. Teuben, J. Organometal. Chem., 74 (1974) 239.
8 F.N. Jones and C.R. Hauser, J. Org. Chem., 27 (1962) 4389.
9 L.E. Manzer, J. Organometal. Chem., 110 (1976) 291.
10 J.H. Teuben, J. Organometal. Chem., 69 (1974) 241.
11 L.E. Manzer and L.J. Guggenberger, J. Amer. Chem. Soc., submitted.
12 M.L.H. Green and C.R. Lucas, J. Organometal. Chem., 73 (1974) 259.
13 R.S.P. Coutts, R.L. Martin and P.C. Wailes, Aust. J. Chem., 24 (1971) 2533.
14 D.F. Evans, J. Chem. Soc., (1959) 2003.
15 R.P.A. Sneeden, F. Glockling and H.H. Zeiss, J. Organometal. Chem., 6 (1966) 194.
16 A.C. Cope and R.N. Gourley, J. Organometal. Chem., 8 (1967) 527.
17 G. van Koten and J.G. Noltes, J. Organometal. Chem.. 82 (1974) C53.
18 A.J. Leusink, G. van Koten, J.W. Marsman and J.G. Noltes, J. Organometal. Chem., 55 (1973) 419.
19 G. Longoni, P. Fantucci, P. Chini and F. Canziani, J. Organometal. Chem., 39 (1972) 413.
20 G. van Koten and J.G. Noltes, J. Organometal. Chem., 102 (1975) 551; G. van Koten, A.J. Leusink and J.G. Noltes, ibid., 85 (1975) 105; G. van Koten, A.J. Leusink and J.G. Noltes, ibid., 84 (1975) 117; G. van Koten and J.G. Noltes, ibid., 84 (1975) 129.