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Preliminary communication

NEW PREPARATION OF ALKYL- AND ARYL-MONO-η^5-CYCLOPENTADIENYLPHOSPHINE COMPOUNDS OF IRON, COBALT AND NICKEL

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Summary

Tertiary phosphine stabilized homoleptic alkyl and aryl compounds of Fe, Co and Ni undergo protonolysis of their M–C bonds with cyclopentadiene to produce the corresponding mono-η^5-cyclopentadienyl complexes. Initial low reaction temperatures and the presence of phosphine ligands prevent the formation of metallocenes. This method allows the easy introduction of various achiral and chiral ligands into complexes of this class.

Cyclopentadienylmetal carbonyl compounds containing σ metal–carbon bonds are generally prepared from metal carbonyls [1,2]. To obtain the corresponding phosphine complexes the cyclopentadienyl halogeno carbonyl species are irradiated in the presence of phosphine ligands [3]. Treatment of the halogeno phosphine compound with an excess of a Grignard reagent finally produces the σ metal–carbon bond [4]. Alternatively, the desired iron compound has been prepared from [CpFe(diphos)(NCCH$_3$)Br] (Cp = C_5H_5, diphos = $Ph_2PCH_2CH_2PPh_2$) [5]. Reaction of lithium, sodium and potassium cyclopentadienides with transition metal halides, MX_n ($n > 1$) gives metallocenes [2]. Thallium cyclopentadienide reacts with [FeCl$_2$(diphos)] in benzene to give a good yield of the mono-η^5-cyclopentadienyliron compound, [CpFe(diphos)Cl] [4]. The same product is formed when thallium cyclopentadienide is substituted for cyclopentadienyllithium or cyclopentadienylmagnesium halides, although the formation of ferrocene becomes more important [6]. It was recently reported that reaction of M(acac)$_2$ (M = Fe, Co, Ni) with C_5Me_5Li in THF gave only the mono-η^5-pentamethylcyclopentadienyl acetylacetonates and no metallocenes [7].

We now have established that the acidic nature of the allyl protons of cyclopentadiene (pK_a 17) readily allows protonolysis of the M–C bonds in thermally unstable homoleptic alkyl compounds of Fe^{II}, Ni^{II} and Co^{II}. In the absence of coordinating phosphine ligands these homoleptic alkyl compounds were found to

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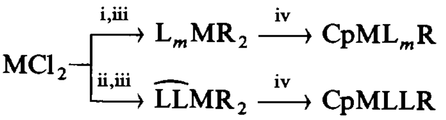
TABLE 1

SYNTHETIC AND CHARACTERIZATION DATA FOR THE COMPLEXES PREPARED

RMgX	Compound	Yield	^{1}H NMR [a]		M^+	Ref.
			(Cp)	(Solvent)		
1 PhMgBr	[η^5-CpFe(diphos)Ph]	61	4.05	CS_2	596	[9]
2 MeMgI	[η^5-CpFe(diphos)Me]	73	4.00	CS_2	534	[4,5,6,10]
3 CH_3CH_2-MgBr	[η^5-CpFe(diphos)CH_2CH_3]	20	4.20	C_6D_6	548	[6]
	[η^5-CpFe(diphos)H]		4.12	C_6D_6	520	[6]
4 PhMgBr	[η^5-CpFe[(R)-prophos]Ph] [b]	40	4.01	CS_2	610	
			4.23	C_6D_6		
5 PhMgBr	[η^5-CpFe$(PMe_3)_2$Ph]	60	3.87	C_6D_6	350.1027 [c]	
6 PhMgBr	[η^5-CpFe($Ph_2P(CH_2)_3$-PPh_2)Ph]	32	4.11	C_6D_6	610	
7 PhMgBr	[η^5-CpNi(PPh_3)Ph]	50			463	[11]

[a] δ (ppm) relative to internal TMS. [b] (*R*)-prophos = *R*-(+)-1,2-bis(diphenylphosphino)propane. [c] Accurate mass; calcd. 350.10138.

react with cyclopentadiene to afford the corresponding metallocenes. Addition of phosphine ligands before the transmetallation reaction of the anhydrous transition metal halides with Grignard reagents, furnished thermally more stable σ-alkyl complexes [8]. The Fe and Ni compounds, nevertheless, still underwent reaction with cyclopentadiene, yielding stable 18-electron phosphine complexes containing one η^5-cyclopentadienyl ligand and one σ metal–carbon bond (Scheme 1).



SCHEME 1. Reagents: (i) mL (L = monodentate tertiary phosphine, $m = 1$ for M = Ni, $m = 2$ for M = Fe); (ii) $\widehat{LL}$ = bidentate tertiary phosphine for M = Fe; (iii) 2RMgX (R = various organic groups, X = Br or I, compare Table 1); (iv) Cp–H.

The compounds prepared according to Scheme 1, and their yields and characterization data, are listed in Table 1. Achiral as well as chiral phosphine ligands (entry 4, Table 1) may be introduced into transition metal complexes by this method. The reactions were performed in either tetrahydrofuran or a 1/1 mixture of toluene and ether. When the alkyl residue contains a β-hydrogen the yields are much lower owing to competing side reactions. Also produced during the preparation of [η^5-CpFe(diphos)CH_2CH_3] (entry 3, Table 1) was the corresponding hydride, [η^5-CpFe(diphos)H], probably via β-hydride migration (compare ref. 6). The 18-electron nickel compound (entry 7, Table 1) could be prepared only in the toluene/ether solvent mixture. The phosphine stabilized homoleptic compounds were prepared at temperatures varying between −60 to 0 °C. The cyclopentadiene substrate was added at −60 °C and the stirred reaction mixtures then allowed to attain room temperature.

The cobalt compound [η^5-CpCoPPh_3Me_2] (III) was prepared similarly form the ate-complex I * in a yield of 60% (Scheme 2). The stable 18-electron complex III was obtained by oxidation of the intermediate cyclopentadienyl-ate complex II *, with either $FeCl_3$ or $[Cp_2Fe][BF_4]$.

$$\begin{tikzcd}
\mathrm{CoCl_2} \arrow[r, "\mathrm{i,ii}"] & {\substack{[\mathrm{Me_3CoPPh_3}]^- \\ (\mathrm{I})}} \arrow[d, "\mathrm{iii}"] \\
{\substack{[\eta^5\text{-}\mathrm{CpCoPPh_3Me_2}] \\ (\mathrm{III})}} & {\substack{[\eta^5\text{-}\mathrm{CpCoPPh_3Me_2}]^- \\ (\mathrm{II})}} \arrow[l, "\mathrm{iv}"']
\end{tikzcd}$$

SCHEME 2. Reagents: (i) PPh_3; (ii) 3MeMgBr; (iii) Cp–H; (iv) $FeCl_3$ or Cp_2Fe^+.

Spectroscopic data for the 18-electron cobalt compound III were identical to those previously published: ^1H NMR ($CDCl_3$): δ 0.06 (d, 2Me, J(PH) 6 Hz); 4.45 (s, Cp) ppm [12,13].

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* The formulae of I and II merely reflect the stoichiometry of the reaction and are not neccessarily the actual structures of the species in solution.