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Preliminary communication

SOME ALKYL OLEFIN COBALT COMPLEXES AND THEIR REACTIONS WITH OLEFINS

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Summary

The complexes $[Co(C_5Me_4Et)LMe_2]$ (I, L = C_2H_4; II, L = C_3H_6; III, L = Ph_3P) are reported, which undergo reactions with olefins. Following olefin exchange, I and II react with C_2H_3R giving $[Co(C_5Me_4Et)(C_2H_3R)_2]$, CH_4 and CH_2CMeR (R = H or Me). The strong stereochemical specificity, together with deuteration experiments and ^1H NMR spectrum of the reaction mixture all point to a simple olefin insertion reaction mechanism. Variable temperature ^1H NMR shows olefin rotation in I.

Olefin insertion into metal—alkyl bonds has long been postulated as the crucial stage in Ziegler—Natta catalysis [1]. However, most isolated transition metal alkyl olefin complexes are perfectly stable [2] and there is to date only one example where such complexes perform this reaction [3]. Consequently, alternative mechanisms for Ziegler—Natta catalysis were proposed involving α-elimination and the formation of metallocyclobutane intermediates [4].

This preliminary communication reports the complexes $[Co(C_5Me_4Et)LMe_2]$, (I, L = C_2H_4; II, L = C_3H_6; III, L = Ph_3P), and their reactions with olefins and phosphines.

The complexes, I and II were prepared by reaction of $[Co_2(C_5Me_4Et)_2Cl_4]$ [5] with 2 mol methyllithium and excess olefin in ether at −78°C. They were purified by elution from a column of Kieselgel 60 at −70°C with ether (see Scheme 2). Complex III was prepared analogously from $[Co(C_5Me_4Et)(Ph_3P)Cl_2\cdot toluene]$ [5] and purified by column chromatography at 10°C. The complexes I—III are all air sensitive and I and II are unstable above −25°C, although excess olefin appears to stabilise them at higher temperatures.

The formulation of I and II is supported by quantitative studies of their reactions in solution. Thus, reaction with Ph_3P gives 1 mol III (by Co analysis and ^{1}H NMR), together with 1 mol of the appropriate olefin (by gas chromatography). Ether or toluene were used as solvents. In addition, ^{1}H NMR and analytical data shown in Tables 1 and 2 were obtained on crystalline samples of I and II, which could be made by slowly evaporating the ether solutions to dryness at −78°C. Complex III was characterised by ^{1}H NMR and mass spectroscopy and elemental analysis. These data are given in Table 1.

Variable temperature ^{1}H NMR at 400 MHz of I with excess C_2H_4 shows that the complexed C_2H_4 resonance is an AA′BB′ pattern at −60°C. On warming to −40°C and then −20°C, however, broadening and then coalescence occur, until at 20°C a single band between the original resonances appears. On recooling to −60°C one obtains the original spectrum. This may be interpreted as evidence for rotation of the olefin (E_a 12.5 kJ mol^{-1}) since the position of the final single band rules out olefin exchange.

Nevertheless, the complexes I and II, may be interconverted by exposure to an excess of the appropriate olefin at 0°C for 5 min, liberating the previously coordinated olefin stoichiometrically (as determined by gas chromatography). Subsequently, over 3 h further reaction occurs giving $[Co(C_5Me_4Et)(C_2H_3R)_2]$ (IV, R = H [5] or V, R = Me, CH_4, and CH_2CMeR', R′ = H or Me, respectively). The products were estimated and identified using gas chromatography, ^{1}H NMR and Co analysis by atomic absorption, and shown to be in stoichiometric proportions. ^{1}H NMR data on IV and V are given in Tables 1 and 2. III gives a similar reaction at ca. 60°C which was similarly established.

TABLE 1

ANALYTICAL DATA FOR COMPOUNDS I AND II

Compound		Color	Analysis (found (calcd.) (%))	*m/e*
$[Co(C_5Me_4Et)(C_2H_4)Me_2]$	I	yellow-brown	Co: 22.0 (22.1)^a	—
$[Co(C_5Me_4Et)(Ph_3P)Me_2]$	III	orange	C: 74.8 (74.4) H: 7.6 (7.6)	500^b

^{a} Error 2% (on figures), the analysis was performed on solid isolated by evaporation of a solution to dryness at low temperature in a preweighed ampoule. ^{b} Very weak, fragmentation observed giving much more intense peaks.

The reaction of I with ethylene was also studied by ^{1}H NMR at 60 and 400 MHz. Resonances due to I vanish over 1 h at 20°C, while new peaks due to CH_4, C_3H_6 and IV appear. No intermediate species were observed.

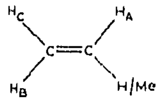
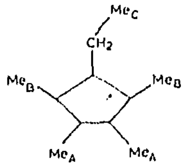
The mechanism of the reaction of I with ethylene was studied by deuteration of the alkyl groups and ethylene. Reaction of $[Co(C_5Me_4Et)(C_2H_4)(CD_3)_2]$ with C_2D_4 gave (by GC/MS) CD_4 and C_3D_6, together with some C_2D_6 by decomposition. Similarly, the same complex with C_2H_4 gave CD_3H and $C_3H_3D_3$ as hydrocarbon products. The $C_3H_3D_3$ was conclusively identified as >95% CH_2CHCD_3 by 400 MHz ^{1}H NMR (see Table 2).

Complex I is closely similar to that proposed by Evitt and Bergmann [6] as an unobserved intermediate in the reaction of $[Co(C_5H_5)(Ph_3P)Me_2]$ with ethylene and the present work is entirely consistent with their reaction mechanism as shown in Scheme 1.

Furthermore, the stereoselective reaction of II with propene giving >90%

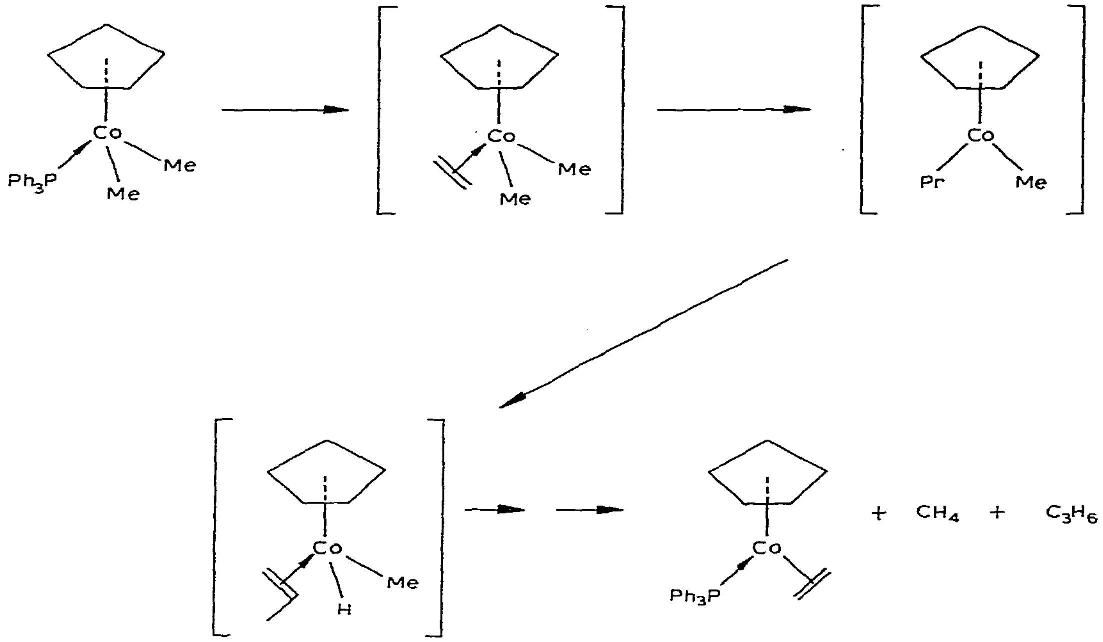
TABLE 2

^{1}H NMR DATA (chemical shifts in δ) AT 400 MHz

Compound															
	Olefin resonances								Cyclopentadienyl resonances					Co–Me	Other
	H_A	H_B	H_C	Me	J_{cis}	J_{trans}	J_{gem}	$J(H_a\text{–}Me)$	CH_2	Me_A	Me_B	Me_C	J(Et)		
$[Co(C_5Me_4Et)(C_2H_4)Me_2]^a$	2.66	1.89	—	—	—	13.5	—	—	1.74	1.30	1.26	0.90	7	0.21	—
$[Co(C_5Me_4Et)(Ph_3P)Me_2]^b$	—	—	—	—	—	—	—	—	1.7	1.3	1.3	0.8	8	0.1^c	7.0 Ph_3P
$[Co(C_5Me_4Et)(C_2H_4)_2]^b$	1.05	1.77	—	—	8.6^e	14.0^e	-0.2^e	—	2.08	1.50	1.42	0.96	7.6	—	—
$[Co(C_5Me_4Et)(C_3H_6)_2]^b$	2.30	0.53	1.83	1.06	8.8	12.8	ca. 0	5.9	2.02	1.44	1.44	0.95	6.9	—	—
$C_3H_6{}^a$	5.70	4.94	4.99	1.57	10.3	16.6	2.0	6.3	—	—	—	—	—	—	—
$CH_2CHCD_3{}^a$	5.71	4.95	5.0	—	9.7	17.0	2.4	1.0^d	—	—	—	—	—	—	

[a] In toluene-d_8. [b] In benzene-d_6. [c] Spectrum at 60 MHz. J(P—H) 6 Hz. [d] H—D coupling. [e] Coupling constants obtained by optimised fit to calculated 2nd order spectrum.

All peaks were integrated and gave the correct relative intensities.



SCHEME 1

CH_2CMe_2 demonstrates that a reaction is occurring under crowded conditions, implying that the metal atom is acting as a mediator. The orientation is the same as that found in Ziegler—Natta catalysis [7] and is the opposite of that normally produced by metals on the right hand side of the transition series [8].

The reactivity of I and II to olefin insertion contrasts with the inertness of $[Co(PMe_3)_3(C_2H_4)R]$ (R = Me or Ph) [2b]. It would seem that the oxidation state of cobalt has some role in determining reactivity. Possibly a high oxidation state of cobalt prevents back donation from the metal to the olefin and this is a prerequisite for insertion.

Table 2 shows the ^1H NMR shifts and coupling constants of free olefins and those coordinated in the complexes described in this note. It can be seen that the comparability of the coupling constants suggests little deformation of the olefin on coordination. This would indeed be consistent with poor back donation by the metal. The large chemical shift changes are thus not felt to be due to a change in the hybridisation of the olefinic carbon, but rather to the proximity of the cobalt atom.

Olefin complexes of the early transition metals, however, show strong deformation of the coordinated olefin and low inter-proton coupling constants [9]. The considerable differences between the chemistries of cobalt and titanium make it dangerous to draw too many comparisons. The system discussed here seems to bear a closer resemblance to systems such as Ni^{II} olefin oligomerisation catalysts [10].

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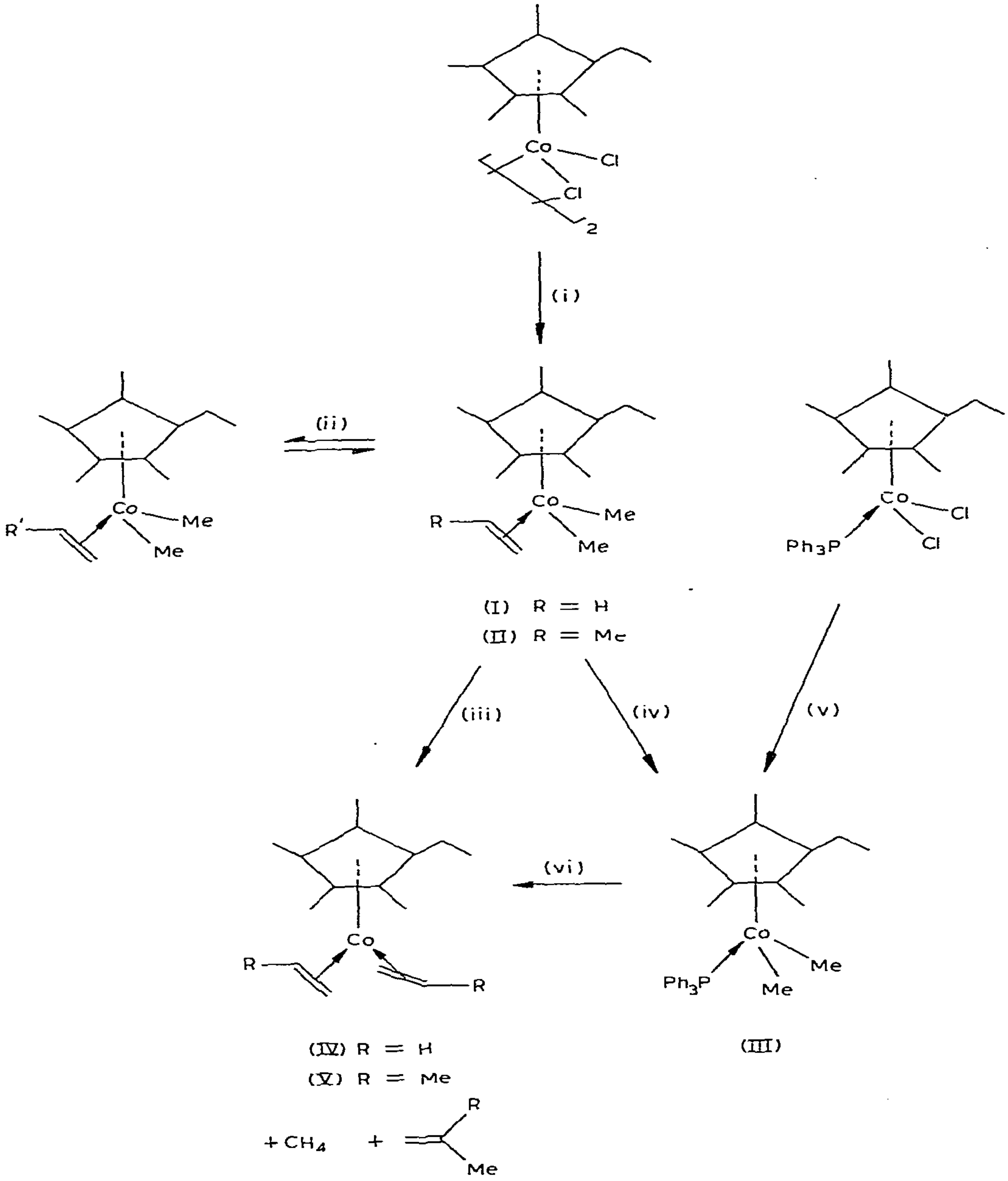

SCHEME 2. (i) 2 mol MeLi, excess C_2H_3R in Et_2O, –78°C, 18 h; (ii) excess C_2H_3R', 0°C, 5 min, R = Me or H, respectively; (iii) excess C_2H_3R, 0°C, 3 h; (iv) excess Ph_3P, 0°C, 1 h; (v) 2 mol MeLi in Et_2O, 0°C, 2 h; (vi) excess C_2H_4 (R = H), 60°C, 10 h.

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References

1 P. Cossee, J. Catal., 3 (1964) 80.
G.W. Parshall, Homogeneous Catalysis, Wiley, New York, 1980, p. 29.
2 For example: (a) C.J. Guggenberger, P. Meakin and F.N. Tebbe, J. Amer. Chem. Soc., 96 (1974) 5420.
(b) H.F. Klein, R. Hammer, J. Gross and U. Schubert, Angew. Chem. Int. Ed. Engl., 19 (1980) 809.
(c) N.J. Cooper and M.L.H. Green, J. Chem. Soc., Dalton, (1979) 1121.
3 R. Cramer, J. Amer. Chem. Soc., 87 (1965) 4717; Acc. Chem. Res., 1 (1968) 186.
4 K.J. Irvin, J.J. Rooney, C.D. Stewart, M.L.H. Green and R. Mahtab, J. Chem. Soc. Chem. Commun., (1978) 604; M.L.H. Green and R. Mahtab, J. Chem. Soc., Dalton, (1979) 262.
5 M.L.H. Green and R.B.A. Pardy, J. Chem. Soc., Dalton, (1979) 1355.
6 E.R. Evitt and R.G. Bergmann, J. Amer. Chem. Soc., 101 (1979) 3973.
7 P. Longi, G. Mazzanti, A. Roggero and A.M. Lachi, Makromol. Chem., 61 (1963) 63; E.J. Arlmann and P. Cossee, J. Catal., 3 (1966) 99.
8 G. Henrici-Olivé and S. Olivé, Coordination and Catalysis, Verlag Chemie, Weinheim, 1977, p. 126 and 190.
9 S.J. Mclain, R.R. Schrock and J. Sancho, J. Amer. Chem. Soc., 102 (1980) 5610; A.J. Schultz, R.K. Brown, J.M. Williams and R.R. Schrock, ibid., 103 (1981) 169; C.G. Kreiter, K. Nist and H. Alt, Chem. Ber., 114 (1981) 1845.
10 R.B.A. Pardy and I.B. Tkatchenko, J. Chem. Soc. Chem. Commun., (1981) 49; P.W. Jolly and G. Wilke, The Organic Chemistry of Nickel, Academic Press, New York, 1974.