Implications of Three-Center, Two-Electron M–H–C Bonding for Related Alkyl Migration Reactions: Design and Study of an Ethylene Polymerization Catalyst

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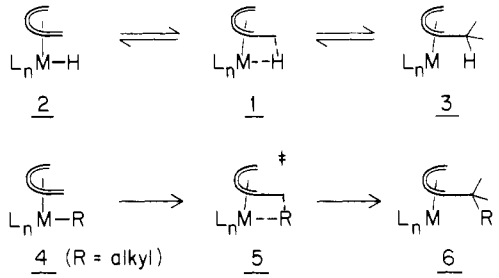
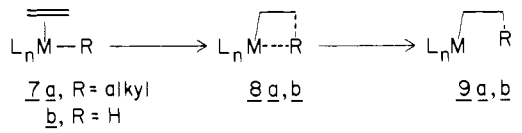
These are now numerous, well-documented cased where alkene–, polyene–, or polyenyl–metal hydride complexes adopt the bridged or agostic structure containing a three-center, two–electron M–H–C bond **1** rather than the classical, terminal hydride structure **2**.[1-5] Such bridged species are invariably in dynamic equilibrium with both **2** and coordinatively unsaturated **3**.



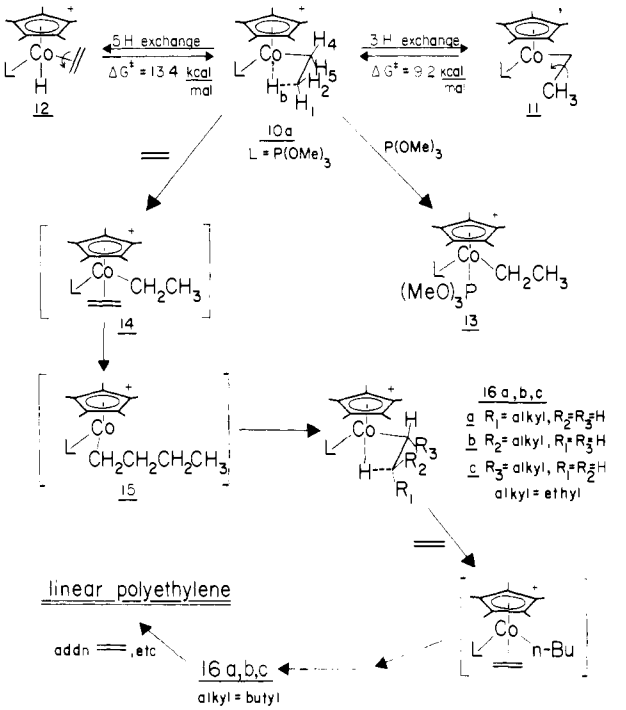
We propose that there exists a parallel between the structure and dynamics of the hydride complexes and the activation energies for alkyl migration reactions of their alkyl analogues, **4** → **6**. The barriers for these alkyl migration reactions will be lower for cases in which the hydride analogues exist as bridged isomers, **1**, rather than terminal hydrides, **2**. *The same factors that favor a bridging over terminal hydride structure will facilitate alkyl migration.* This concept is useful for predicting which metal alkyl olefin complexes will undergo facile migratory insertion reactions or, more generally, the feasibility of any carbon–carbon bond-forming reactions arising from metal-to-ligand alkyl migrations. Application of this idea in the design and study of an ethylene polymerization catalyst is described here.

The migratory insertion reaction of metal alkyl olefin complexes **7a** → **9a** has been postulated as the key step in Ziegler–Natta



polymerizations (Cossee–Arlman mechanism[6]). Alternative mechanistic proposals have been advanced, stimulated in part by the absence of simple stoichiometric models for **7a** → **9a**.[1,7,8] None

Scheme I



of the many isolated *cis*-alkyl ethylene complexes undergoes migratory insertion reactions.[9,10] Examination of NMR data, where available, for the hydride analogues of these $L_nM(C_2H_4)R$ complexes shows[9afgh,11] (1) each hydride analogue has a *terminal hydride structure*, **7b**, and (**2**), in general, activation energies for *hydride* migrations **7b** → **9b** are greater than ca. 17 kcal/mol. Since alkyl migrations generally have higher activation energies than hydride migrations, it follows that migratory insertion fails to occur in these $L_nM(C_2H_4)$(alkyl) systems because of large activation barriers.

In order to test our hypothesis, we have generated an ethylene alkyl complex whose hydride analogue is bridged. In accord with our general proposal we find that (1) the alkyl migration reactions are quite facile and (2) the system serves as an effective ethylene polymerization catalyst.

The "ethylene hydride" complexes **10** (L = C_2H_4, $P(C_6H_4R)_3$, $P(CH_3)_3$) adopt agostic structures.[4,5] We have prepared the trimethyl phosphite complex **10a** whose bridged hydride structure is verified by ^1H and ^{13}C NMR data, most diagnostic is the low J_{CH_b} = 61 hz.[12] Dynamic ^1H and ^{13}C NMR studies of **10a**

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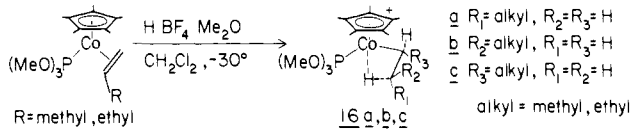
0002-7863/85/1507-1443$01.50/0

establish a three-proton exchange process (H_b,H_1,H_2, $\Delta G^{\ddagger}$ = 9.2 kcal/mol) via methyl group rotation and a five-proton exchange process (H_b,H_1,H_2,H_3,H_4, $\Delta G^{\ddagger}$ = 13.4 kcal/mol) consistent with formation of the ethylene hydride **12** accompanied by ethylene rotation.[13] Treatment of **10a** with $P(OMe)_3$ results in displacement of the C-H bridge and formation of **13**, a reaction typical of M-H-C systems.[14] Similarly, treatment of **10a** with ethylene should yield **14**, an alkyl(alkene) analogue of **10a**. If alkyl migration is rapid as postulated, **10a**, should catalyze ethylene polymerization by successive migratory insertion reactions. In fact, treatment of **10a** under ethylene pressure yields *linear* polyethylene (-7 °C, CH_2Cl_2, 40 psi C_2H_4, 850 turnovers in 70 h with catalyst remaining active).

Following this ethylene polymerization by ^1H NMR (3 equiv of C_2H_4, CD_2Cl_2, -40 °C), in spite of the spectroscopic complexity, is quite informative. As **10a** disappears with ethylene consumption, no ethylene ethyl complex **14** could be detected. Instead, three new resonances assigned to new bridging hydride species appear at δ -11.8, -12.9, and -13.1 in the ratio 8:12:80, respectively. As polymerization proceeds the methylene resonance at δ 1.2 intensifies but the three briding hydride signals remain essentially unchanged in intensity and relative ratios. The δ 3.2-1.6 region is quite complex.

Scheme I is consistent with our experimental observations. The three new hydride signals have been assigned (see below) to mono-*n*-alkyl substituted isomers of **10a** retaining the bridging hydride structures, i.e., **16a-c** (R = alkyl with R = ethyl the first-formed homologue). These must result from ethyl (or subsequently *n*-butyl, *n*-hexyl, etc.) migration (**14** → **15**) followed by bridging of the β-hydrogen of the new alkyl ligand to the metal center. Operation of the exchange processes delineated for **10a** results in scrambling the alkyl group to the three observed positions.

To support these assignments, equilibrating complexes **16a-c**



have been independently generated by protonation of $(C_5Me_5)(P(OMe)_3)Co(CH_2{=}CHR)$, where R = Me or Et.[15] ^1H and ^{13}C NMR spectra are simplified in that the mixture of homologues arising from differing numbers of ethylene insertions are not present. A key observation is that for R = ethyl there are three bridging hydride signals whose chemical shifts and ratios are identical with those observed in the ethylene polymerization studies. The isomer ratios and chemical shifts of the R = methyl isomers are nearly identical with those of the R = ethyl complexes; thus the positions of the bridging hydride signals appear insensitive to alkyl chain length. For R = CH_3, complete assignments for ^1H and ^{13}C resonances were obtained.[12] Spin saturation transfer experiments confirm the dynamic processes that interconvert the various structural isomers[12] and prove that for (propyl)-$(Me_5C_5)Co(P(OMe)_3)^+$ the two predominant isomers have the methyl group attached to C_β (**16a,b**) with the methyl bound to C_α in the minor isomer, **16c**.

Following the polymerization by ^{13}C NMR confirms Scheme I. Monitoring the ratios of **10a**:**16**(alkyl = $-C_2H_5$):**16** (alkyl = C_4H_9, C_6H_{13}, etc.) shows that the first insertion (**10a** → **16** (alkyl = ethyl)) is *slower* than subsequent insertions.

Three further aspects of this scheme are noted: (1) since under our experimental conditions no alkyl alkene complexes (e.g., **14**) were directly observed, bridged structures **16** are the "resting state" of the catalyst, (2) independent entry into **14** (reaction of $P(OMe)_3$ with **10**, L = C_2H_4) leads initially to **10a** and ethylene which suggests the migration step **14** → **15** is rate determining, and (3) only linear polyethylene forms so only (*n*-alkyl)(ethylene) complexes ultimately undergo migratory insertion even though branched alkyl substituents could arise from reaction of **16c** with ethylene. Although more complex mechanisms[1,7,8] for the insertion reaction cannot be ruled out by these experiments, we favor migratory insertion as the simplest most reasonable mechanism particularly in view of our initial hypothesis.

The principles outlined here are being applied to identify and investigate other alkene polymerization catalysts and carbon-carbon bond forming reactions in metal alkyl polyene complexes.

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Registry No. Polyethylene, 9002-88-4; $(C_5Me_5)(P(OMe)_3)(C_3H_7)CoBF_4$, 94644-97-0; $(C_5Me_5)(P(OMe)_3)(C_4H_9)CoBF_4$, 94644-99-2; $(C_5Me_5)(P(OMe)_3)(C_2H_4)Co$, 94645-00-8; $(C_5Me_5)(P(OMe)_3)(C_3H_6)Co$, 94645-01-9; $(C_5Me_5)(P(OMe)_3)(C_4H_8)Co$, 94645-02-0; $(C_5Me_5)(P(OMe)_3)(C_2H_5)CoBF_4$, 94669-93-9.

Supplementary Material Available: Dynamic NMR of **10a** and ^1H and ^{13}C NMR characterization of **16a-c** (R = methyl, ethyl) and C_5Me_5 $(P(OMe)_3)(C_2H_3R)$ (R = H, CH_3, C_2H_5) (5 pages). Ordering information is given on any current masthead page.

(12) **10a** (prepared via $HBF_4{\cdot}Me_2O$ reaction with C_5Me_5 $(P(OMe)_3)Co(C_2H_4)$ at -30 °C, CH_2Cl_2): ^1H NMR (-70 °C, CD_2Cl_2) δ -12.1 (m, H_b), -0.3 (m, H_1 or H_2), -0.2 (m, H_1 or H_2), 1.9 (m, H_4 or H_5), 2.5 (m, H_4 or H_5); ^{13}C NMR (-90 °C, CD_2Cl_2) δ -5.8 (t d, J_{CH} = 152, J_{CH} = 61 Hz, C_2), 8.3 (q, J = 129 Hz, $C_5\mathit{Me}_5$), 26.5 (t, J = 160 Hz, C_1), 52.0 (q, J = 147 Hz, OMe), 96.8 (s, C_5Me_5).

(13) For details see supplementary material.

(14) **13**: ^1H NMR (-10 °C, CD_2Cl_2) δ 0.95 (t, J = 6 Hz, CH_3), 1.34 (tt, J = 6, J_{HP} = 5 Hz, CH_2), 1.55 (t, J = 3 Hz, $C_5\mathit{Me}_5$), 3.73 (t, J = 5 Hz, OMe); $^{13}C[^1H]$ NMR (-50 °C, CD_2Cl_2) δ 7.0 (t, J_{CP} = 25 Hz, C_1), 9.2 (s, $C_5\mathit{Me}_5$), 18.5 (s, CH_2CH_3), 52.8 (s, OMe), 99.3 (s, C_5Me_5).

(15) Prepared by reaction of $C_5Me_5Co(CH_2CHR)_2$ with $P(OMe)_3$ in analogy with preparations of $C_5Me_5(L)Co(C_2H_4)$: Beevor, R. G.; Frith, S. A.; Spencer, J. L. *J. Organomet. Chem.* **1978**, *221*, C25.

Penem Synthesis through C_3-N Ring Closure of a β-Lactam Precursor

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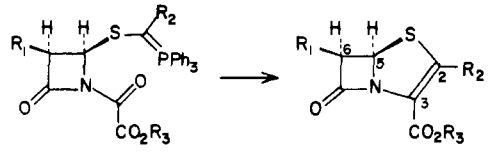
The search for β-lactam antibiotics possessing enhanced activity, satisfactory stability, and resistance to β-lactamases has generated continuing strong interest in methods of preparing the penem system.[1] The early Woodward procedure for constructing this framework made use of an intramolecular Wittig reaction for forming the C_2-C_3 bond[2] (**1** → **2**) and this has remained the



principal method for fusing the five-membered ring to the β-lactam nucleus in the formation of **2**.

Unlike the results obtained in the carbapenem series, the route to penems through C_3-N bond formation has, up to the present, not shown promise. Thus, recent approaches to **2** starting from precursors **3**,[2a] **4**,[3] and **5**[4] have all failed to give C_3-N ring closure.[5]

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