Articles

Mutual Exchange and Isomerization Processes in the Three Isomers of the Mixed-Metal Triangular Cluster Complex $[Re_2Pt(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$

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Received April 11, 1990

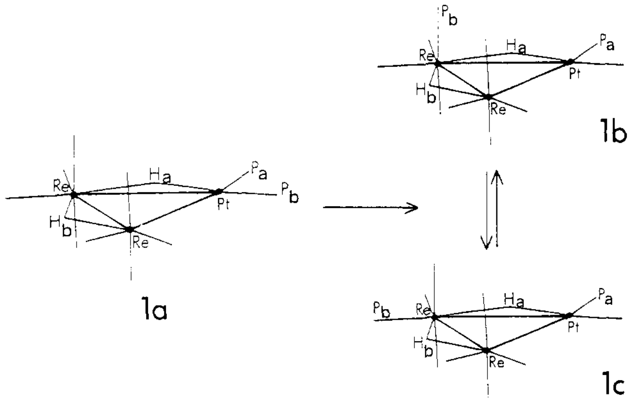
The dynamic processes operative in the three isomers of the triangular cluster $[Re_2Pt(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$ (1) have been studied. ^1H and ^{31}P variable-temperature NMR spectra of the isomer **1a** (in which both the phosphines are bound to Pt) indicate the presence of two mutual exchange processes: one, operative at lower temperature, exchanges only the phosphines, while the second one, active above 238 K, exchanges the hydrides. Computer simulations of the spectra allowed the activation parameters to be calculated (E_a = 49.2 ± 1.4 and 60.2 ± 1.3 kJ/mol, respectively). The isomer **1a** at $T > 273$ K irreversibly rearranges, by the exchange of a phosphine and a carbonyl between Pt and Re, giving the equilibrium mixture of the two isomers **1b** and **1c** (differing in the location of the phosphine bound to Re): this slow first-order reaction has been studied at three temperatures in a conventional kinetic experiment (284-294 K, E_a = 80 ± 7 kJ/mol). 2D EXSY experiments on ^{31}P spectra (295-316 K) and computer simulations of $^1H\{^{31}P\}$ spectra (333-363 K) have been employed to measure the rate of interconversion between the isomers **1b** and **1c**, and the activation parameters (E_a = 74.0 ± 1.7 kJ/mol) have been estimated accordingly. ^{13}C variable-temperature NMR spectra suggest a localized scrambling of the carbonyls in the $Re(CO)_3PPh_3$ moiety of **1b**.

Introduction

The rational approach to the synthesis of trimetallacyclopropane compounds, developed by the Stone group,[1] allowed[2] the addition of the ethylene-like molecule $[Re_2(\mu\text{-}H)_2(CO)_8]$ to the carbenoid fragment $[Pt(PPh_3)_2]$, affording, at 273 K, the triangular cluster complex $[Re_2Pt(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$ (compound **1a** of Scheme I). This compound irreversibly rearranges at higher temperature, through the exchange of a phosphine and a carbonyl between platinum and one rhenium atom, giving the two interconverting isomers **1b** and **1c** (Scheme I). The three compounds have been characterized by ^1H, ^{31}P, and ^1H-detected ^{195}Pt NMR spectroscopy, and the solid-state structure of **1b**, which is the main species in solution at room temperature, was established by an X-ray single-crystal analysis.[2] Scheme I shows the most likely structure for isomer **1c**, on the basis of the NMR data.[2] The ^1H and ^{31}P chemical shifts and the relevant coupling constants concerning the three isomers are reported in Table I.

In solution, the ligands in these molecules exhibit different types of dynamic behavior, the study of which is the object of the present work. Some of the rearrangements involving **1a** are degenerate, and the molecule in the final state is indistinguishable from the starting one (mutual exchange processes).[3] In other cases, the exchanges are not degenerate and lead to the interconversion of isomers.

Scheme I



The rate constants of these processes span ca. 8 orders of magnitude; thus, different techniques were used in order to obtain the kinetic parameters.

Results and Discussion

Variable-temperature ^1H and ^{31}P NMR spectra showed that **1a** is fluxional. In the $^{31}P\{^1H\}$ NMR spectra, as the temperature was increased, the resonances of the two phosphines broadened and coalesced (Figure 1a): first the low-field Pt satellites (ca. 235 K), then the central signals (ca. 260 K), and eventually the high-field satellites, since the temperature of coalescence increases with the effective chemical shift separation. The observed behavior indicates the following: (i) The spin-spin correlations between Pt and P are retained during the process of exchange. That is, there is no dissociation of the P ligands. (ii) The coupling constants with ^{195}Pt of both P atoms are of the same

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[1] Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89 and references therein.

[2] Beringhelli, T.; Ceriotti, A.; D'Alfonso, G.; Della Pergola, R.; Ciani, G.; Moret, M.; Sironi, A. *Organometallics* **1990**, *9*, 1053.

[3] See for instance: (a) Jesson, J. P.; Meakin, P. *Acc. Chem. Res.* **1973**, *6*, 269. (b) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982; p 6.

Table I. NMR Data for the Three Isomers of $[Re_2Pt(\mu-H)_2(PPh_3)_2(CO)_8]$ (CD_2Cl_2; 273 K for 1b and 1c, 188 K for 1a)

	chem shift, ppm[a]				coupling const, Hz[b]						
compd	H_a	H_b	P_a	P_b	H_a–P^c	H_b–P^c	H_a–Pt	H_b–Pt	P_a–Pt	P_b–Pt	P_a–P_b
1a	−9.22	−15.62	25.3	15.2	12.8		502		2167	4142	16.5
					82.3						
1b	−6.71	−14.31	44.4	14.5	14.2	3.0	668	35	2625	43	
					11.8	13.2					
1c	−7.42	−14.82	41.9	15.0	18.8	...	534	32	2517	130	
					3.5	18.6					

[a] ^{31}P chemical shifts are downfield positive with respect to H_3PO_4. [b] Absolute values. [c] The first row of H–P values refers to P_a and the second row to P_b.

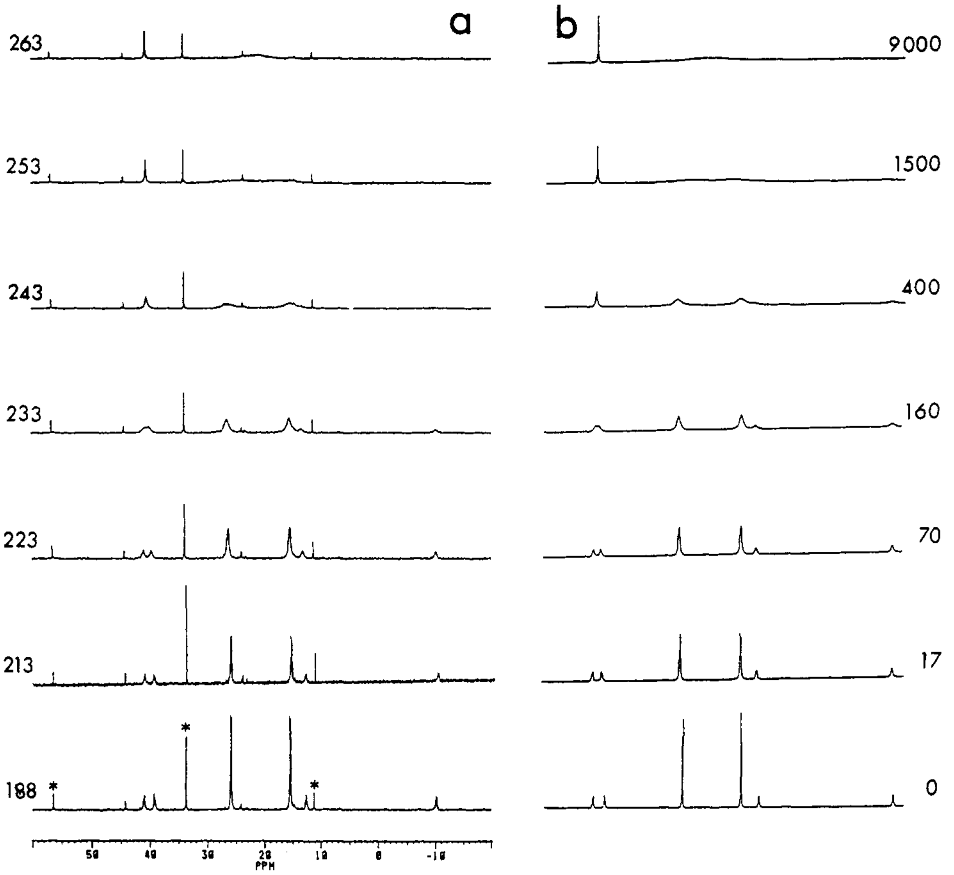


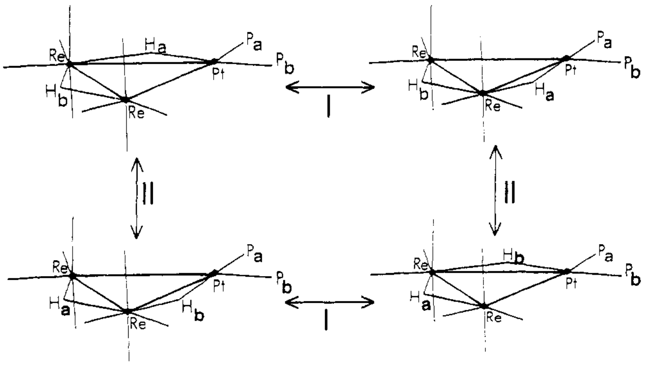
Figure 1. $^{31}P\{^1H\}$ variable-temperature NMR spectra of **1a** (resonances of the parent $[Pt(PPh_3)_2(C_2H_4)]$ are marked with asterisks): (a) observed (temperature/K); (b) computer simulated (k/s^{-1}).

sign. Computer simulations of the $^{31}P\{^1H\}$ NMR spectra (Figure 1b) allowed the calculation of the kinetic constants reported in Figure 1.

The hydridic region of the ^1H NMR spectra is reported in Figure 2a. For the low-field resonance (due to H_a bridging the Pt–Re bond), in the range 200–233 K, the outer lines of the doublet of doublets broadened and collapsed, the inner ones remaining sharp. The same behavior was observed in its ^{195}Pt satellites. The evolution of these signals toward triplets (due to the growth, in their centers, of the averaged signals corresponding to the "near-fast" exchange of the outer lines) was accompanied, at temperatures above 233 K, by the broadening of all the components of the multiplets, as well as of the H_b resonance, and eventually by their collapse at 273 K.

The low-temperature behavior of the H_a resonance is a well-known phenomenon,[4] indicative of (i) a mutual exchange process (presence of invariant lines) and (ii) the opposite sign of the coupling constants of H_a with the two phosphorus atoms (coalescence of the external components of the multiplet), as previously shown by 2D ^1H–^{195}Pt reverse correlation experiments.[2] A similar behavior was observed in various other complexes containing $HM(PR_3)_n$ moieties (M = transition metal).[4,5]

Scheme II



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[4] Jesson, J. P.; Mutterties, E. L. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: London, 1975.

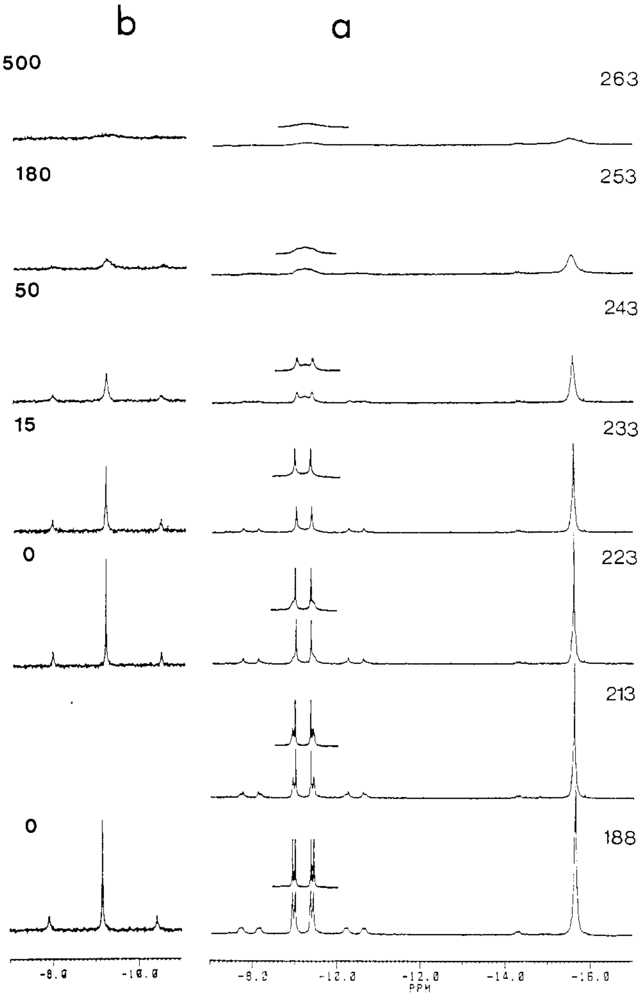

Figure 2. (a) Hydridic region of the ^1H variable-temperature (K) NMR spectra of **1a**. Computer simulations of the low-field resonances are shown in the insets. (b) H_a region of the $^1H\{^{31}P\}$ variable-temperature NMR spectra of **1a**, with the rate constants calculated from the computer simulations (k/s^{-1}).

Attempts to reproduce the ^1H variable-temperature NMR spectra with use of the rate constants obtained for the exchange of the phosphines failed. Variable-temperature $^1H\{^{31}P\}$ NMR spectra were therefore recorded in order to perform an independent evaluation of the rates of hydride exchange. These spectra (the H_a resonance is reported in Figure 2b with the rate constants obtained by computer simulations) showed that the hydridic resonances did not change up to 233 K.[6] The difference between the two sets of kinetic constants required to fit the $^1H\{^{31}P\}$ and the $^{31}P\{^1H\}$ NMR spectra indicates that two different exchange processes are operative. The simulations of the ^{31}P-coupled ^1H spectra, allowing for both the processes, gave satisfactory results (Figure 2a, inset).

The hopping of the hydride from one Pt–Re edge to the other (process I in Scheme II) is the easiest way in which the permutation of the phosphines can be achieved. This kind of process is not observed in the isomers **1b** and **1c** (vide infra), probably because in these species, as already reported in related systems,[7] a cis coordination between the hydride and the phosphine bound to the platinum atom is preferred, in order to relieve the steric repulsion between this phosphine and the equatorial carbonyl bound to rhenium. In **1a**, this demand could also be the driving force of process II, as shown in Scheme II. According to this mechanism, at higher temperatures, H_b could also move to a bridging location between Pt and Re, with the simultaneous transfer of H_a to the Re–Re edge. This process equalizes both the hydrides and the phosphines, but its contribution to the mutual exchange observed at low temperature is negligible, because its rate is about 1 order of magnitude lower than the other one.

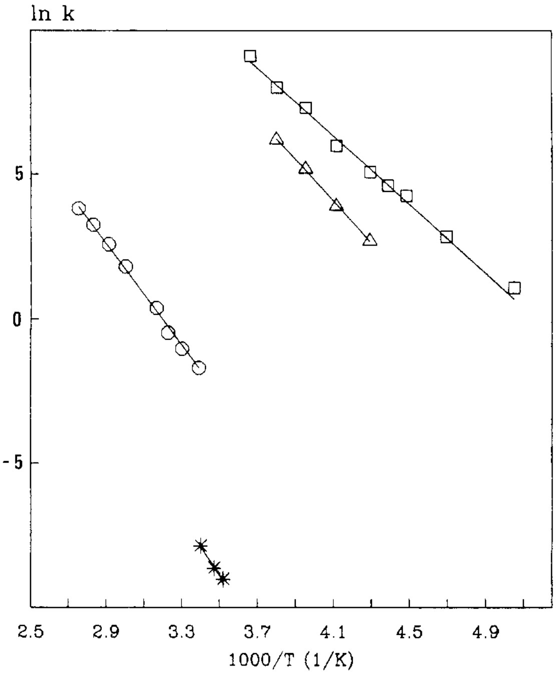

Figure 3. Arrhenius plots of the rate constants determined for the dynamic processes of the isomers **1a**, **1b**, and **1c**: (□) exchange of the phosphines in **1a**; (△) exchange of the hydrides in **1a**; (*) irreversible isomerization **1a** → **1b** + **1c**; (○) reversible isomerization **1b** $\rightleftarrows$ **1c**.

The activation parameters for the exchange of the phosphines and of the hydrides were obtained through least-squares fits of Arrhenius (Figure 3) and Eyring plots of the kinetic constants derived from the simulation of ^{31}P and $^1H\{^{31}P\}$ NMR spectra: $E_a = 49.2 \pm 1.4$ kJ mol^{-1}, $\Delta H^\ddagger = 46.7 \pm 1.4$ kJ mol^{-1}, $\Delta S^\ddagger = 0.8 \pm 5.8$ J mol^{-1} K^{-1} and $E_a = 60.2 \pm 1.3$ kJ mol^{-1}, $\Delta H^\ddagger = 58.0 \pm 1.3$ kJ mol^{-1}, $\Delta S^\ddagger = 28.8 \pm 5.1$ J mol^{-1} K^{-1}, respectively.

At higher temperatures, one phosphine and one carbonyl (as shown in Scheme I) are irreversibly exchanged between platinum and one rhenium atom. The reaction is slow enough to be monitored by the growth of the ^1H NMR signals of the isomers **1b** and **1c** (those of **1a** being almost completely collapsed at temperatures between 273 and 300 K). The ratio **1b**/**1c** was always constant, indicating that the rate of the interconversion of the isomers is higher than that of their formation (vide infra). We could not establish, therefore, the kinetically preferred isomer. Plots of ln ($C_\infty - C$) vs time (where C_∞ and C are the concentrations of either **1b** or **1c**; see Experimental Section) were satisfactorily linear up to more than 75% of conversion, and least-squares fits allowed the determination of the first-order rate constants at 284, 288, and 294 K and accordingly

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(5) See for instance: (a) Azizian, H.; Dixon, K. R.; Eaborn, C.; Pidcock, A.; Shuaib, N. M.; Vinaixa, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1020. (b) Bars, O.; Braunstein, P.; Geoffroy, G. L.; Metz, B. *Organometallics* **1986**, *5*, 2021.

(6) The $^1H\{^{31}P\}$ spectra revealed a small, not completely resolved, coupling with ^{195}Pt of the hydride bridging the Re–Re bond, H_b (J_{H-Pt} = 18 Hz), which was accounted for in the computer simulations.

(7) Farrugia, L. J.; Green, M.; Hankey, D. R.; Murray, M.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1985**, 177.

a rough estimation of the activation energy (80 ± 7 kJ mol^{-1}, Figure 3).

The irreversibility of the reaction **1a** → **1b** + **1c** can be justified by both steric and electronic factors: indeed in **1b** and **1c**, minor steric repulsion between the equatorial ligands on different metals and more equalized charge distribution in the cluster are achieved. Similar intermetallic CO/PR_3 exchanges were reported for carbonyl clusters of the iron triad[8] and for heterobimetallic μ-phosphido complexes.[9] In particular, platinum-assisted CO labilization reactions have been recently observed.[10] In heterobimetallic M–Pt systems[10b] evidence has been presented supporting a pathway involving PPh_3 dissociation from Pt and CO transfer from M to Pt via a μ-CO intermediate. A similar mechanism cannot be ruled out in the present case, even if the experimental E_a value seems too low for a pure dissociative mechanism.

The last type of dynamic process investigated quantitatively is the interconversion **1b** ⇄ **1c**. In the temperature range 295–320 K, the rate of this process lies in a range suitable to be studied by means of 2D exchange spectroscopy (2D EXSY),[11] but at higher temperatures (330–363 K) the exchange is fast enought to allow the use of the band-shape analysis of the hydridic resonances.

As is the case for all methods that use the transfer of magnetization in order to detect chemical exchange, 2D EXSY is useful when the rate constant of the process is smaller than the transverse relaxation rate, but greater than/or on the same order as the longitudinal relaxation rate ($R_1 < k < R_2$ where $R_1 = 1/T_1$ and $R_2 = 1/T_2$). For the isomerization **1b** ⇄ **1c**, the 2D NMR experiments were performed on ^{31}P, because of the longer T_1 compared to that of the hydrides, the simpler pattern of the cross-peaks, and the unlikely presence of cross-relaxation phenomena. The experiments were performed in the phase-sensitive mode, since in this way the appearance of a cross-peak with the same phase as the diagonal ones is indicative of a chemical exchange process.[11] In the present case, owing to the overlap of the diagonal and cross-peaks for the high-field resonances (P_b bound to Re in **1b** and **1c**, Figure 4), the exchange is proved by the presence of cross-peaks between the P_a resonances of two isomers (phosphines bound to Pt). The analysis of the data matrix was therefore restricted to these resonances, and the process was treated as an exchange between two sites with different populations.

The evolution of the resonances in a 2D EXSY experiment is described by the matrix **L** (the sum of the relaxation and kinetic matrices), the elements of which are defined as $l_{ii} = -(T_2)_i^{-1} - \sum k_{ij}$ and $l_{ij} = k_{ji}$, provided cross relaxation is absent. The experimental intensities of the cross and diagonal peaks (the matrix **I** of the experimental results) are related to the matrix **L** according to

$$\mathbf{J} = \mathbf{I}\cdot\mathbf{P}^{-1} = C \exp(\mathbf{L}\tau_m)$$

where **P** is the diagonal population matrix, C is a scaling constant, and τ_m is the mixing time used for the experiment. Diagonalization of the matrix **J** allows the calculations of the kinetic constants of the exchange process from the off-diagonal elements of the matrix **L**:[12]

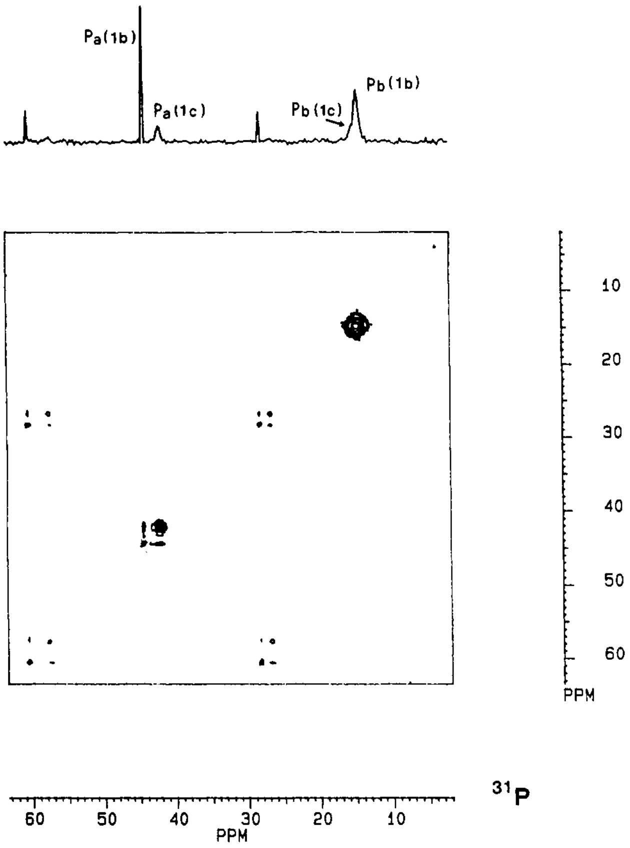

Figure 4. Contour plot of a ^{31}P 2D EXSY experiment (295 K, mixing time 1.2 s, toluene-d_8). A total of 32 transients of 512 data points were collected over a spectral width of 5000 Hz for 64 increments in t_1. Zero-filling in F_1 and weighting functions ($\pi/2$ shifted sine bell in F_2 and Gaussian in F_1) were applied before transformation. The spectrum reported on the top is a projection of the 2D intensity map.

$$C \exp(\mathbf{L}\tau_m) = \mathbf{V}\cdot\Lambda\cdot\mathbf{V}^{-1}$$

$$\mathbf{L} = (\tau_m)^{-1}(\mathbf{V}\cdot(\ln \Lambda)\cdot\mathbf{V}^{-1} - \ln C)$$

where **V** and Λ are the matrices of the eigenvectors and of the eigenvalues of **J**, respectively.

Using this procedure and allowing for the population change with the temperature,[2] we calculated the kinetic constants at four different temperatures, as detailed in the Experimental Section.

At temperatures higher than 330 K, sizable broadening was observed in the hydridic resonances (Figure 5). $^1H\{^{31}P\}$ spectra were recorded every 10 K from 333 to 363 K, and their computer simulations gave the values of the rates of the isomerization. Figure 3 shows that these values and those computed from 2D EXSY lie satisfactorily on the same Arrhenius straight line (E_a = 74.0 ± 1.7 kJ mol^{-1}, $\Delta H^{\ddagger}$ = 71.4 ± 1.7 kJ mol^{-1}, and $\Delta S^{\ddagger}$ = −17.4 ± 5.2 J mol^{-1} K^{-1}).

The isomerization **1b** ⇄ **1c** most likely occurs through an intramolecular pathway. In fact (i) 2D EXSY experiments both on ^1H (available as supplementary material

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(8) (a) Bruce, M. J.; Shaw, G.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1082. (b) *Ibid.* **1972**, 1781.

(9) (a) Jones, R. A.; Lasch, J. G.; Norman, N. C.; Stuart, A. L.; Wright, T. C.; Whittlesey, B. R. *Organometallics* **1984**, *3*, 114. (b) Breen, M. J.; Shulman, P. M.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* **1984**, *3*, 782.

(10) (a) Wang, S. J.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 3233. (b) Powell, J.; Gregg, M. R.; Sawyer, J. F. *Inorg. Chem.* **1989**, *28*, 4451. (c) *Ibid.* **1989**, *28*, 4461 and references therein. (d) Powell, J.; Fuchs, E.; Gregg, M. R.; Phillips, J.; Stainer, V. R. *Organometallics* **1990**, *9*, 387. (e) Beringhelli, T.; D'Alfonso, G. Manuscript in preparation.

(11) (a) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546. (b) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Clarendon Press: Oxford, U.K., 1985; Chapter 9 and references therein.

(12) (a) Perrin, C. L.; Gipe, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 4036. (b) Abel, E. W.; Coston, T. P. J.; Orrell, K. G.; Sik, W.; Stephenson, D. *J. Magn. Reson.* **1986**, *70*, 34. (c) Beringhelli, T.; D'Alfonso, G.; Molinari, H.; Hawkes, G. E.; Sales, K. D. *J. Magn. Reson.* **1988**, *80*, 45.

in ref 2) and on ^{31}P show that there is no loss of spin correlation in the HPtPPh$_3$ moiety (there are no cross-peaks among the central signals and the satellites both within and between the isomers), (ii) both the hydrides of **1b** and H$_b$ in **1c**[13] retain their couplings with P$_b$, until the exchange itself causes the broadening of their signals (T > 330 K), ruling out any fast ($k \approx J_{\text{H-P}}$) dissociative behavior of P$_b$, (iii) the addition of a different phosphine (PMe$_2$Ph) at room temperature resulted in the instantaneous substitution *only* of the phosphine bound to Pt[14] (probably via an associative pathway on the nearly square-planar platinum atom), ruling out a dissociative behavior of P$_b$ with the same rate as the **1b** $\rightleftarrows$ **1c** exchange ($k \approx 0.2$ s^{-1} at 295 K), and (iv) the small and *negative* value of $\Delta S^{\ddagger}$ (−17.4 J mol^{-1} K^{-1}) is inconsistent with a dissociative mechanism.

If the structure of the isomer **1c** is the one depicted in Scheme I, this isomerization can be described as the change from a *fac* to a *mer* arrangement of the carbonyls of the Re(CO)$_3$PPh$_3$ moiety, occurring possibly through a localized restricted trigonal twist on the Re atom.

Variable-temperature ^{13}C NMR spectra of a ^{13}CO-enriched sample of **1b**/**1c** indicated that another fluxional process is operative in **1b**.[15] Instead of the eight signals expected on the basis of the solid-state structure, the room-temperature spectrum showed only five main peaks (192.3, 190.5, 189.5, 188.9, and 188.8 ppm, respectively). When the temperature was lowered, some new resonances appeared, but extensive broadening at lower temperatures (even in natural-abundance samples) prevented any sound assignments. Also, variable-temperature selective ^{1}H decouplings were of little aid: the irradiation of H$_a$ clearly affected only the signal of the carbonyl bound to Pt (188.9 ppm, $J_{\text{C-Pt}}$ = 1735 Hz, $J_{\text{C-P}}$ = 4 Hz, $J_{\text{C-H}}$ = 30 Hz, values in the range observed in analogous compounds).[16] The irradiation of H$_b$ sharpened only the signal at 190.5 ppm ($J_{\text{C-Pt}}$ = 30 Hz, $J_{\text{C-H}}$ = 4 Hz), showing that, for most carbonyls, $J_{\text{C-H}}$ is negligible. The absence of any resolved coupling to ^{31}P of the four resonances observed at 294 K for the Re$_2$ moiety suggests that the signals of the Re(CO)$_3$PPh$_3$ unit are collapsed. The exchange **1b** $\rightleftarrows$ **1c** is too slow to be responsible for this. The process does not affect the resonances of the hydrides and the phosphines, and therefore it must be a mutual exchange, most likely a localized scrambling of the three carbonyls of the Re(CO)$_3$PPh$_3$ unit.

In this hypothesis, therefore, two kinds of ligand scrambling processes localized on the P-bearing Re atom would be operative in **1b**, possibly both via a restricted trigonal twist: one involving carbonyls and the phosphine, leading to the isomerization **1b** $\rightleftarrows$ **1c**, and the other one involving only the carbonyl ligands, the latter being the lower energy process. The easier mobility of the ligands on the Re(CO)$_3$PPh$_3$ moiety with respect to that for the Re(CO)$_4$ species it is not surprising, because it has already been reported[17] that substitution of a carbonyl by a phosphorus ligand lowers the activation energies of both localized and delocalized scrambling of the carbonyls. In the present case, owing to the presence of the bridging hydrides, the delocalized scrambling is prevented.

Experimental Section

Synthesis of the ^{13}C-Enriched Sample. The synthesis was performed as previously described,[2] with use of a ^{13}CO-enriched sample of [Re$_2$(μ-H)$_2$(CO)$_8$], prepared from [Re$_2$(CO)$_{10}$], about 25% ^{13}CO enriched by UV irradiation (Philips HPK 125-W lamp, Pyrex filtered) for 150 min under a CO atmosphere (90% ^{13}C).

NMR Measurements. The spectra were recorded on a Bruker AC200 spectrometer operating at 200.13, 81.015, and 50.327 MHz for ^{1}H, ^{31}P, and ^{13}C, respectively. ^{1}H{^{31}P} spectra were recorded by use of a B-SV3 unit with a second synthesizer and an amplifier allowing up to 80 W of decoupling power. The temperature was controlled by the B-VT1000 equipment of the spectrometer, which ensures a precision of ±1 K. For the variable-temperature experiments on **1a**, the accuracy of the measurements was first checked by calibration with a MeOH/MeOD solution. ^{1}H, ^{31}P, and ^{1}H{^{31}P} spectra were recorded one after the other on the same sample at each temperature. The temperature of the measurements on the irreversible transformation of **1a** and of the 2D EXSY experiments on the isomerization **1b** $\rightleftarrows$ **1c** was checked before and after the experiments. For the spectra of the mixture **1b**/**1c** at 333–365 K, the temperature was calibrated with C$_2$H$_4$O$_2$/(CD$_3$)$_2$SO. The solutions used were typically 0.05 M in CD$_2$Cl$_2$; for the 2D EXSY experiments and variable-temperature spectra of the mixture **1b**/**1c** the solvent used was toluene-d_8, to allow a more favorable ratio of **1c** vs **1b**[2] and to extend the range of temperature for the experiments.

The program DNMR3[18] was used for the simulations of the ^{31}P spectra (where second-order effects are present for the low-field ^{195}Pt satellites) and the ^{1}H{^{31}P} spectra of **1a**; separate calculations were run for the satellites and the central resonances. The high-field resonance in the ^{31}P spectra showed a linear temperature dependence of the chemical shift, which was accounted for in the simulations. Since homonuclear couplings are absent in the ^{1}H spectra and the ^{31}P spectra of the isotopomer with nonactive Pt are first-order spectra, the ^{1}H-coupled spectra of this isotopomer were simulated by treating each resonance as independent, with use of the program MSEX (multisite exchange).[19] The uncertainty of the kinetic constants derived is ca. 10%. MSEX was also used for the simulations of the ^{1}H{^{31}P} high-temperature spectra for the isomerization **1b** $\rightleftarrows$ **1c**, which gave the following values: 6 (333 K), 13 (343 K), 25 (353 K), 45 (363 K) s^{-1}.

The irreversible isomerization of **1a** could not be followed through the disappearance of its resonances, which collapsed at the relevant temperatures. However, since the ratio of the two isomers **1b** and **1c** is constant ($[\mathbf{1c}]/[\mathbf{1b}] = R$) and the reaction is almost quantitative (i.e. $[\mathbf{1a}]_0 = [\mathbf{1b}]_\infty + [\mathbf{1c}]_\infty = (1 + R)[\mathbf{1b}]_\infty$), the usual first-order kinetic law can be recast as $\ln([\mathbf{1b}]_\infty - [\mathbf{1b}]_t) = \ln([\mathbf{1b}]_\infty) - kt$, $[\mathbf{1b}]_\infty$ being the final concentration of the major isomer and $[\mathbf{1b}]_t$ the concentration at the time t. The spectral parameter used to estimate [**1b**] was the mean of the heights of the peaks of the doublet at high field (−14.28 ppm), and the final values were extrapolated by the plot of the intensities vs time. The rate constants were calculated by a standard least-squares fitting and gave correlation coefficient ranging from 0.999 to 0.995: (1.17 ± 0.02) × 10^{-4}, (1.70 ± 0.02) × 10^{-4}, and (3.64 ± 0.03) × 10^{-4}

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(13) In the range 273–313 K the resonances of *only* the isomer **1c** showed an anomalous broadening, accompanied by the loss of the coupling H$_a$–P$_b$ (not recovered at higher temperatures). This behavior, which is not accounted for by the isomerization process (too slow at these temperatures) or by some other fluxional process of the phosphine ligands (it is observed also in the ^{1}H{^{31}P} spectra), could indicate the presence of a hidden exchange partner.

(14) Addition of 1 equiv of PMe$_2$Ph to a solution of **1b** and **1c** in toluene-d_8 at room temperature resulted in the instantaneous formation of the new compound [Re$_2$Pt(μ-H)$_2$(PPh$_3$)(PMe$_2$Ph)(CO)$_8$], with the entering ligand bound to Pt. In fact, in the ^{31}P NMR spectrum (δ 15.3 (J_{PPt} 2473 Hz) and 16.0 ppm) only the signal coupled with Pt was markedly shifted with respect to the corresponding resonances in **1b** or **1c** (δ 44.9 or 43.0 in toluene), while the ^{1}H spectrum presented the same pattern of hydridic resonances as in **1b**, the resonance due to the H bound to Pt being shifted upfield more than the other one (δ −7.12 (dd, J_{HP} = 12 and 15 Hz, J_{HPt} = 658 Hz) and −14.08 (d, J_{HP} = 13 Hz, J_{HPt} = 34 Hz)). This species was unstable in solution, due to the presence of free PPh$_3$, causing the formation of ReH(CO)$_4$PPh$_3$ (as observed also for **1b**/**1c**), through a reaction path still under investigation.

(15) The amount of **1c** in the solvent used (tetrahydrofuran-d_8) is low enough[2] to attribute to **1b** alone the main features of the spectra.

(16) Ewing, P.; Farrugia, L. J.; Rycroft, D. S. *Organometallics* **1988**, *7*, 859.

(17) See for instance: (a) Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Schorpp, K. T. *J. Chem. Soc., Dalton Trans.* **1976**, 1403. (b) Deeming, A. J.; Donovan-Mtunzi, S.; Kabir, S. E.; Manning, P. J. *J. Chem. Soc., Dalton Trans.* **1985**, 1037. (c) Alex, R. F.; Pomeroy, R. K. *Organometallics* **1987**, *6*, 2437.

(18) Kleier, D. A.; Binsch, G. *J. Magn. Reson.* **1970**, *3*, 146.

(19) Chan, S. O.; Reeves, L. W. *J. Am. Chem. Soc.* **1973**, *95*, 673.

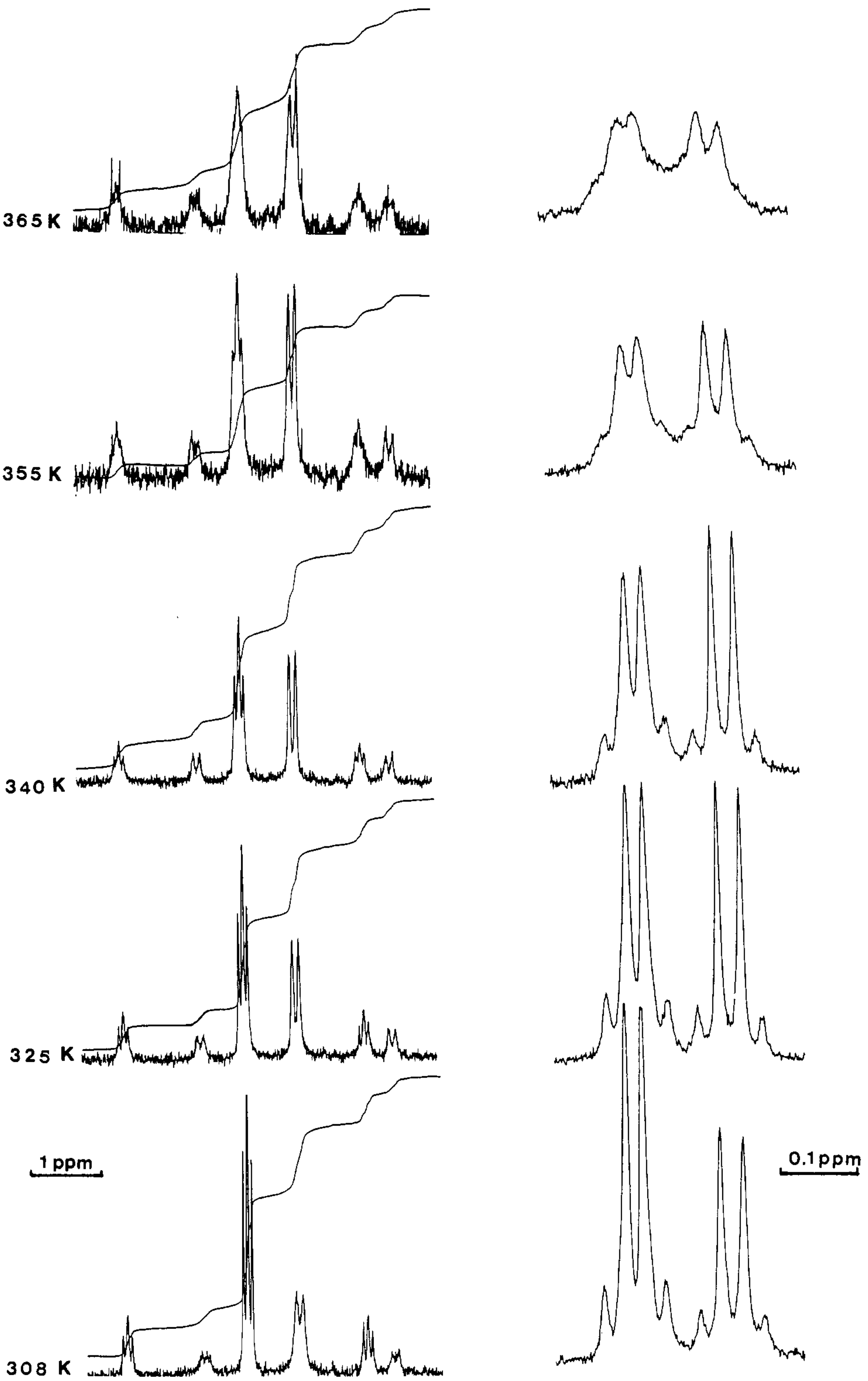

Figure 5. Hydridic regions (left, H_a; right, H_b) of the ^1H variable-temperature NMR spectra for a toluene-d_8 solution of **1b** and **1c**.

s^{-1} at 284, 288, and 294 K, respectively.

The 2D EXSY experiments were performed in the phase-sensitive mode in order to check the absence of cross-relaxation phenomena. The mixing times used were in the range 1.5–0.4 s. At 295 K two experiments were performed with two different mixing times (1.2 and 1.5 s) and the rate constants derived were the same, within the experimental uncertainties. The relative populations of the two species at each temperature were evaluated from the integrated intensity ratio of the hydridic signals. The intensity data from the 2D map were estimated from the volume of the peaks, as given by the routine of the spectrometer. For the experiments at 295 K the evaluation was made also by summing the integrals of the resonances in the relevant cross-sections: the rate constants derived were the same within the experimental error. The variances of the rate constants were calculated by following the procedure suggested by Kuchel et al.,[20] with 6% and 3% as upper estimates of the uncertainties in the volume and the population measurements, respectively. The calculated values are the following: 0.185 ± 0.015 s^{-1} (τ = 1.2 s, 295 K), 0.184 ± 0.015 s^{-1} (τ = 1.5 s, 295 K), 0.364 ± 0.030 s^{-1} (τ = 0.8 s, 303 K), 0.623 ± 0.049 s^{-1} (τ = 0.5 s, 311 K), and 1.47 ± 0.13 s^{-1} (τ = 0.4 s, 316 K).

The least-squares fits of the Arrhenius and Eyring plots were made with a locally written program that allows for uncertainties

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[20] Kuchel, P. W.; Bulliman, B. T.; Chapman, B. E.; Mendz, G. L. *J. Magn. Reson.* **1988**, *76*, 136.

in both the dependent and independent variables.[21]

Acknowledgment. We thank the Progetto Finalizzato Chimica Fine II of the Italian CNR for financial support and instrumental facilities.

Registry No. 1, 126063-64-7.

Supplementary Material Available: Figures giving variable-temperature $^{1}H\{^{31}P\}$ NMR spectra of **1a** and their computer simulations and variable-temperature $^{13}C\{^{1}H\}$ NMR spectra of an equilibrium mixture of the isomers **1b** and **1c** (2 pages). Ordering information is given on any current masthead page.

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(21) Irvin, J. A.; Quickenden, T. I. *J. Chem. Educ.* **1983**, *60*, 712.

Solvolysis of Dimethylzirconocene by Trialkylaluminum Compounds

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Received May 15, 1990

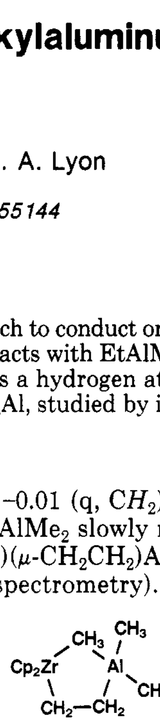
Liquid metal alkyls are strong Lewis acids and bases and useful solvents in which to conduct organometallic reactions. Cp_2ZrMe_2 undergoes rapid methyl exchange with pure Me_3Al but reacts with $EtAlMe_2$ in Me_3Al to form $Cp_2Zr(\mu\text{-}CH_3)(\mu\text{-}CH_2CH_2)AlMe_2$. Neat R_3Al reagents in which R has a hydrogen atom produce solvated Cp_2ZrH_2 derivatives. The gas-phase reaction of $Cp_2ZrCH_3^+$ with Me_3Al, studied by ion cyclotron resonance spectrometry, produces an ion formulated as $Cp_2Zr(\mu\text{-}CH_2)_2Al^+$.

Study of highly concentrated protic acids in which the conjugate bases are but weakly coordinated has been a highly productive area of chemistry. Notable is $HSO_3F{\cdot}SbF_5$, commonly known as magic acid.[1] In an analogous context, liquid metal alkyls such as Me_6Al_2, Me_3Ga, and Me_2Zn can serve both as powerful Lewis acids and bases as well as solvents. They are well suited to NMR experiments and, because of their high reactivity, are easily obtained free of dissolved oxygen and water; indeed, they are self-cleaning. The reactivity of alkyl derivatives of group IV metallocenes with aluminum alkyls is of interest on account of the ability of such systems to catalyze the polymerization of olefins.[2] We report here the reactions of Cp_2ZrMe_2 ($Cp = \eta^5\text{-}C_5H_5$) with some trialkylaluminum compounds, R_3Al, in fluid solution and discuss the effect of the structure of R on reactivity patterns. We also present complementary data on analogous gas-phase chemistry as studied by ion cyclotron resonance (ICR) spectrometry.

Solution-Phase Chemistry

^{13}C NMR spectroscopy shows that, in 0.3 M toluene solution, there occurs a facile ($\Delta G^{\ddagger} = 16.7$ kcal mol^{-1}) statistical scrambling of $^{13}CH_3$ groups in $Cp_2Zr(^{13}CH_3)_2$ with the methyl groups in $(CH_3)_6Al_2$.[3] However, no new products or intermediates are detectable. We reasoned that these might be observed with the help of mass action if neat Me_3Al were used as both solvent and reactant. In fact, a new reaction has been detected but it is due to $EtAlMe_2$ present as an impurity at a 2.2 mol % level in commercial Me_3Al that is recognizable by its ^1H signals at 1.00 (t, CH_3) and −0.01 (q, CH_2) ppm.[4]

In neat Me_3Al, $EtAlMe_2$ slowly reacts with Cp_2ZrMe_2 to form $Cp_2Zr(\mu\text{-}CH_3)(\mu\text{-}CH_2CH_2)AlMe_2$ (**1**) and methane (identified by mass spectrometry). In hydrocarbon solvents, **1** decomposes too rapidly to permit growth of single crystals but its structure and composition can be deduced beyond cavil from spectroscopic and analytical data. The ^{13}C NMR spectrum of **1** exhibits a single Cp resonance at 107.2 ppm ($J_{CH} = 173$ Hz; $\delta(^1H)$ 5.30 ppm). The Zr–C-H$_3$–Al bridging methyl group is associated with a peak at −21.5 ppm ($J_{CH} = 115$ Hz; $\delta(^1H)$ −0.79 ppm). The high-field chemical shift is in accord with those observed in crystallographically characterized compounds known to contain a Zr–CH$_3$–Al bridge.[5] The Zr–CH_2 portion of the Zr–CH$_2$–CH$_2$–Al ethylene bridge gives rise to a ^{13}C resonance at 33.7 ppm ($J_{CH} = 144$ Hz; cf. Cp_2ZrMe_2, $\delta(^{13}C)$ 30.7, $J_{CH} = 117$ Hz), and the −CH_2–Al terminus is associated with a resonance at 1.39 ppm ($J_{CH} = 127$ Hz). The respective ^1H chemical shifts of the two types of CH_2 are 1.07 and −0.08 ppm. These protons, H_A and H_X, respectively, give rise to an AA′XX′ multiplet, simulation of which yields $J_{XX'} = -12$ Hz, $J_{AX} = 13.2$ Hz, and $J_{AX'} = 6.8$ Hz. The proton spectrum provides evidence that the two methylene units are bonded to one another in the same molecule (vide infra). ^{13}C NMR measurements yield second-order rate constants for formation of **1** of 0.98 and



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(1) Olah, G. A. *Super Acid Chemistry*; Wiley: New York, 1985.

(2) (a) Kaminsky, W.; Hahnsen, H. U.S. Patent 4,544,762. (b) Kaminsky, W.; Miri, M. *J. Polym. Sci. Polym. Chem. Ed.* **1985**, *23*, 2151. (c) Kaminsky, W.; Kulper, K.; Brintzinger, H.-H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (d) Sinn, H.; Kaminsky, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *19*, 390.

(3) Siedle, A. R.; Newmark, R. A.; Lamanna, W. M.; Schroepfer, J. N. *Polyhedron* **1990**, *9*, 301.

(4) We write the chemical formula for dilute Et_3Al in Me_3Al as if it were a single compound, $EtAlMe_2$. In fact, it is likely a statistical mixture of dimers in which $(EtAlMe_2)_2$ is most abundant. Similarly, for simplicity, we write R_3Al as such, even though it may be predominantly a dimer in solution.

(5) Waymouth, R. M.; Santarsiero, B. D.; Coots, R. J.; Bronikowski, M. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 1427.

0276-7333/91/2310-0400$02.50/0