

nicotinamide analogue, (N-Et)BNA⁺ (Table I). The bis(nicotinamide) complexes are presumably constrained to a limited number of conformations by their linkages, decreasing the possibility of an optimal side-by-side interaction.

In conclusion, the present work reveals the importance of side-by-side coherent arrangement of CT donor and acceptor for enhancement of their mutual interaction, which is otherwise not effective in aqueous systems. Even though bis(nicotinamide)-type CT acceptors undergo somewhat enhanced interaction with π donors relative to the corresponding mononicotinamide through intramolecular cooperation of two nicotinamide moieties, such ternary CT complex formation is remarkably enhanced in single-compartment vesicles that lead to the formation of CT complex aggregates. The tight side-by-side arrangement of amphiphile molecules due to their hydrophobic and hydrogen-belt interactions forces CT donor molecules to be placed in the proximity sites of acceptor moieties and to come into close contact with them upon desolvation when donor molecules are incorporated. Such molecular organization favorable to CT interaction is further advanced by additional electrostatic interaction among donor and acceptor molecules on the vesicular surface. Such highly organized molecular assemblies can be utilized as effective reaction fields that are able to enhance various reactions due to so-called proximity effects. Single-compartment vesicles involving amino acid residues as molecular components are quite promising molecular assemblies for this purpose.

Registry No. 1, 87-51-4; 2, 120-72-9; (NA)⁺C₅Ala2C₁₂, 81388-56-9; (N-Et)BNA⁺, 81388-57-0; bis(N-Et)BNA⁺, 81388-58-1; bis(C₆BNA⁺), 81408-01-7.

Complexity in the Reductive Reaction of CoCl₂ in the Presence of Phosphites. Isolation of Stable, Noninterconvertible Co[P(OCH₃)₃]₄ and Co₂[P(OCH₃)₃]₈ Molecules

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We have found that the reduction of cobalt(II) chloride by sodium amalgam in the presence of triisopropyl phosphite in tetrahydrofuran solution yielded HCo[P(O-*i*-C₃H₇)₃]₄ and Co₂[P(O-*i*-C₃H₇)₃]₈ in an approximate molar ratio of 2:1. This result was initially interpreted by us, in partial analogy to cobalt carbonyl chemistry, as a primary generation of a Co[P(O-*i*-C₃H₇)₃]₄ radical, which then either dimerized or abstracted a hydrogen atom from a solution-state species. However, this seemingly plausible mechanistic rationale is untenable. In the analogous trimethyl phosphite system, we have now isolated and fully characterized the monomer Co[P(OCH₃)₃]₄ and the dimer Co₂[P(OCH₃)₃]₈ and have further shown that they do not interconvert. Neither monomer nor dimer abstracts hydrogen atoms from organic solvents

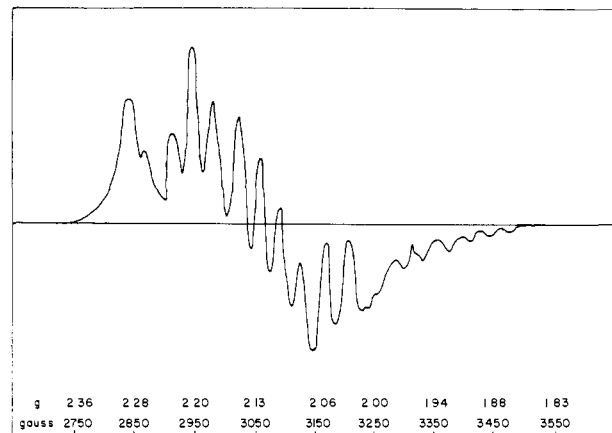
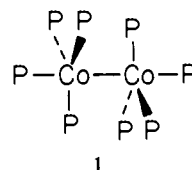


Figure 1. The electron spin resonance spectrum of Co[P(OCH₃)₃]₄ in a toluene glass at -196 °C shows a $g_{\perp} = 2.099$ and $g_{\parallel} = 2.149$ with hyperfine coupling constants (cm⁻¹) of $|A_{\parallel}(\text{Co})| = 0.0072$, $|A_{\perp}(\text{Co})| = 0.0037$, $|A_{\perp}(\text{P}_1)| = 0.08$, $|A_{\parallel}(\text{P}_1)| = 0.0104$, and $|A_{\parallel}(\text{P}_2-\text{P}_4)| \approx 0.00055$. This spectrum was originally observed and analyzed by F. J. Hirsekorn and K. Zamaraev in our laboratories at Cornell University in 1975, but the composition of the complex was not defined at that time nor were single crystals obtained. The analysis of the spectral details presented here is based on the earlier studies with slightly better resolved spectra obtained at -196 and -160 °C in toluene and toluene-*d*₈ glasses.

or reacts with hydrogen (H₂) until temperatures of 50–90 °C. There are, in fact, rather striking differences between the phosphite and the carbonyl chemistry of zerovalent or monovalent cobalt complexes as established by our studies described herein.

Reduction of cobalt(II) chloride by 2 equiv of sodium amalgam in the presence of excess triisopropyl phosphite in tetrahydrofuran at 25 °C produced HCo[P(O-*i*-C₃H₇)₃]₄² and Co₂[P(O-*i*-C₃H₇)₃]₈ in respective yields of 54% and 46% (based on cobalt equivalents).⁴ The dimer is a novel, remarkable species, with eight bulky isopropyl phosphite ligands, which has an axially bridged bi(trigonal bipyramidal) form, **1**, as established by the solution-state NMR



studies.⁵ In sharp contrast, the analogous reduction⁶ in the presence of excess trimethyl phosphite produced as major products the new trigonal-bipyramidal Co[P(O)(OCH₃)₂][P(OCH₃)₃]₄ complex,⁷ the mercurial Hg{Co[P(OCH₃)₃]₄}₂,^{8,10} and an unusual salt, {Co[P(OCH₃)₃]₅⁺}[Co[P(OCH₃)₃]₄Na{(CH₃O)₃P]₄Co⁻}¹³ in respective yields⁴ of ~20%, 20%, and 50%. Only small amounts of HCo[P(OCH₃)₃]₄⁸ and CH₃Co[P(OCH₃)₃]₄⁸ and none of the

(2) For original synthesis and characterization data, see ref 3.

(3) (a) Muetterties, E. L.; Watson, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 6978. (b) Rakowski, M. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 739.

(4) All yields reported here are in terms of cobalt atom equivalents.

(5) ³¹P{¹H} NMR (toluene-*d*₈, -70 °C) δ 183.3 (eq P, d, $J_{\text{PP}} = 73$ Hz, 3), 245 (ax P, q, $J_{\text{PP}} = 73$ Hz, 1). All ³¹P data are referenced to 85% H₃PO₄.

(6) See Supplementary Material for synthesis procedure.

(7) Anal. Calcd for CoC₁₄H₄₂O₁₅P₅: C, 25.31; H, 6.39; P, 23.31. Found: C, 25.68; H, 6.29; P, 23.04. ¹H NMR (CD₃C₆D₅, 35 °C) δ 3.55 (complex m); ³¹P{¹H} NMR (CD₃C₆D₅, -70 °C; A = ax P(OCH₃)₃, B = eq P(OCH₃)₃, C = ax P(O)(OCH₃)₂) δ 169.09 (A, second-order d of quar, $J_{\text{AB}} = 137.6$ Hz, $J_{\text{AC}} = 275.2$ Hz, 1), 154.09 (B, t, $J_{\text{AB}} = 137.6$ Hz, $J_{\text{BC}} = 137.6$ Hz, 3), 109.87 (C, overlapping d of quar, $J_{\text{AC}} = 275.2$ Hz, $J_{\text{BC}} = 137.6$ Hz, 1); ³¹P{¹H} NMR (CD₃C₆D₅, 27 °C) δ 155.9 (A and B, br, s, 4), 107.5 (C, br, s, 1).

(8) For the original synthesis and characterization of this complex see ref 9.

(9) Muetterties, E. L.; Hirsekorn, F. J. *J. Am. Chem. Soc.* **1974**, *96*, 7920.

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$\text{Co}_2[\text{P}(\text{OCH}_3)_3]_8$ dimer, previously prepared⁸ from $\text{KCo}[\text{P}(\text{OCH}_3)_3]_4$ and $(\text{CH}_3)_3\text{GeCl}$, were detected or isolated. The complex salt is based on an anion generated by the solvation of a sodium ion by three phosphite oxygen atoms in two $\text{Co}[\text{P}(\text{OCH}_3)_3]_4^-$ anion complexes.¹⁴ Decomposition of this complex salt occurred slowly in tetrahydrofuran solution at 20 °C to produce the insoluble salt $\text{Na}^+[\text{Co}[\text{P}(\text{OCH}_3)_3]_4]^-$,¹⁵ the trigonal-bipyramidal $\text{Co}[\text{P}(\text{O})(\text{OCH}_3)_2][\text{P}(\text{OCH}_3)_3]_4$ complex, and the tan monomeric $\text{Co}[\text{P}(\text{OCH}_3)_3]_4$ radical in high yields.¹⁷ The monomeric $\text{Co}[\text{P}(\text{OCH}_3)_3]_4$ species was paramagnetic and exhibited an ESR spectrum (toluene glass at -196 °C) qualitatively interpretable as a $d^9 C_{3v}$ CoP_4 complex (Figure 1). An X-ray crystallographic investigation¹¹ of a crystal of $\text{Co}[\text{P}(\text{OCH}_3)_3]_4$ was attempted, but crystal quality and disorder phenomena precluded a precise, structural analysis.¹⁸ Nevertheless, the crystallographic data were fully consistent with a C_{3v} tetrahedral CoP_4 framework.¹⁹

(10) (a) A crystallographic study¹¹ of this mercurial, to be reported separately, established a geometry and stereochemistry analogous to $\text{Zn}[\text{Co}(\text{CO})_4]_2$ and $\text{Hg}[\text{Co}(\text{CO})_4]_2$ with trigonal-bipyramidal geometry about each cobalt atom, a linear $\text{P}_{ax}\text{CoHgCoP}_{ax}$ array (Co-Hg-Co , 180°; Hg-Co-P_{ax} , 178.9 (2)°), a staggered arrangement of the two CoP_4 units about the mercury atom, a tipping of the two equatorial P_3 planes toward the mercury atom, and distance parameters of 2.676 (2) Å for Co-Hg , 2.139 (5) Å for Co-P_{ax} and 2.127 (5, 8, 11, 3) Å¹² for Co-P_{eq} . (b) Lee, B.; Burlitch, J. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1967**, *89*, 6362. (c) Sheldrick, G. M.; Simpson, R. N. *F. J. Chem. Soc. A* **1968**, 1005.

(11) X-ray crystallographic structure determinations were performed for $\text{Hg}[\text{Co}[\text{P}(\text{OCH}_3)_3]_4]_2$ and $\text{Co}[\text{P}(\text{OCH}_3)_3]_4$. Intensity measurements for both compounds were made on a Nicolet PL autodiffractometer using full (1.0° wide) ω scans and graphite-monochromated $\text{Mo K}\alpha$ radiation. Both structures were solved and refined on a Data General Eclipse S-200 computer using locally modified versions of the Nicolet E-XTL interactive crystallographic software system. Space group and unit cell data for the two compounds are as follows: monoclinic, space group $P2_1/n$ [an alternate setting of $P2_1/c-C_2^2$ (No. 14)] with $a = 9.897$ (4) Å, $b = 14.386$ (3) Å, $c = 17.414$ (4) Å, $\beta = 94.88$ (3)°, and $Z = 2$ (formula units) for $\text{Hg}[\text{Co}[\text{P}(\text{OCH}_3)_3]_4]_2$; rhombohedral, space group $R\bar{3}C_2$ (No. 146) with $a = 9.227$ (6) Å, $\alpha = 107.61$ (5)°, and $Z = 1$ for $\text{Co}[\text{P}(\text{OCH}_3)_3]_4$. Unit-weighted full-matrix least-squares refinement of the structural parameters for $\text{Hg}[\text{Co}[\text{P}(\text{OCH}_3)_3]_4]_2$ with anisotropic thermal parameters for Hg, Co, and P atoms and isotropic thermal parameters for O and C atoms resulted in R (unweighted, based on F) = 0.063 for 2464 independent reflections having $2\theta_{\text{MoK}\alpha} < 43^\circ$ and $I > 3\sigma(I)$. The Hg atom occupies the crystallographic inversion center at the origin of the unit cell. Unit-weighted full-matrix least-squares refinement of the structural parameters for the Co and P atoms of $\text{Co}[\text{P}(\text{OCH}_3)_3]_4$ gave $R = 0.214$ for 339 independent reflections having $2\theta_{\text{MoK}\alpha} < 43^\circ$ and $I > 3\sigma(I)$. The failure of carbon and oxygen atoms to appear in the difference Fourier calculated at this point indicated severe disordering of all phosphite methoxy arms and was consistent with the observation of a rapid decline in scattering from the crystal with increasing Bragg angle. The Co and one P atom lie on a crystallographic C_3 axis.

(12) The first number in parentheses following an averaged value of a bond length or angle is the root mean square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements that are included in the averaged value.

(13) (a) Anal. Calcd for $\text{Co}_3\text{C}_9\text{H}_{11}\text{O}_9\text{P}_3\text{Na}$: C, 25.84; H, 6.52; P, 22.21; Na, 1.27. Found: C, 26.61; H, 6.37; P, 22.38; Na, 1.21. $^{31}\text{P}\{\text{H}\}$ NMR (tetrahydrofuran- d_6 , -70 °C) δ 153–149.4 (a complex series of lines (A_2B_2 spectrum) characteristic^{13b} of $\text{Co}[\text{P}(\text{OCH}_3)_3]_4^+$). No signal was observed for the phosphorus nuclei in the anion, presumably due to unfavorable relaxation effects arising from the quadrupolar cobalt nucleus. ^1H NMR (tetrahydrofuran- d_6 , 35 °C) δ 3.65 (m, 5), 3.35 (m, 8). (b) $[\text{Co}[\text{P}(\text{OCH}_3)_3]_5^+]\text{Cl}^-$ was synthesized by stirring CoCl_2 and $\text{P}(\text{OCH}_3)_3$ with activated magnesium in tetrahydrofuran. The $^{31}\text{P}\{\text{H}\}$ NMR spectrum of $[\text{Co}[\text{P}(\text{OCH}_3)_3]_5^+]$ prepared in this way was identical with the $^{31}\text{P}\{\text{H}\}$ spectrum of $[\text{Co}[\text{P}(\text{OCH}_3)_3]_5^+][\text{Co}[\text{P}(\text{OCH}_3)_3]_4\text{Na}[(\text{CH}_3\text{O})_3\text{P}]_4\text{Co}^-]$. The ^{31}P NMR spectrum of $[\text{Co}[\text{P}(\text{OCH}_3)_3]_5^+]$ has been studied by Meakin and Jesson^{13d} for a tetraphenylborate salt. We found the chemical shifts of the two types of phosphorus atoms in the cation to be a function of solvent (as well as temperature). Maximal chemical shift separations were achieved with an acetone- d_6 solution at -80 °C: $\delta_{\text{P}_{ax}}$ 154.2; $\delta_{\text{P}_{eq}}$ 150.5, $J_{\text{P}_{ax}\text{P}_{eq}}$ = 140.6 Hz. Neither our δ values nor our J values corresponded precisely with those of Meakin and Jesson,^{13c} but the solvents were different and the associated anions were different. The values reported by Meakin and Jesson for the $\text{B}(\text{C}_6\text{H}_5)_4^-$ salt in CHCl_2 at -138 °C were $\delta_{\text{P}_{ax}}$ -11.5, $\delta_{\text{P}_{eq}}$ -5.0 ($\text{P}(\text{OCH}_3)_3$ reference) and $J_{\text{P}_{ax}\text{P}_{eq}}$ = 148 Hz. (c) Meakin, P.; Jesson, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 5751. (d) Jesson, J. P.; Meakin, P. *J. Am. Chem. Soc.* **1974**, *96*, 5760.

(14) Alternatively, the salt could be formulated as a double salt $[\text{Co}[\text{P}(\text{OCH}_3)_3]_5^+][\text{Co}[\text{P}(\text{OCH}_3)_3]_4^-]$ and $\text{Na}^+[\text{Co}[\text{P}(\text{OCH}_3)_3]_4^-]$. However, the simple sodium salt is insoluble in tetrahydrofuran, whereas this curious salt is quite soluble in tetrahydrofuran. Solubilization of alkali metal salts of $[\text{Co}[\text{P}(\text{OCH}_3)_3]_4^-]$ has been observed before as in the hydrocarbon soluble salt $\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3\text{Na}^+[\text{Co}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4^-]$.^{3b} Single crystals of $[\text{Co}[\text{P}(\text{OCH}_3)_3]_5^+][\text{Co}[\text{P}(\text{OCH}_3)_3]_4\text{Na}[(\text{CH}_3\text{O})_3\text{P}]_4\text{Co}^-]$ were obtained. Because diffraction quality was not high and because the unit cell has one very long edge of ~ 80 Å, a structural analysis was not achieved. A rational structural representation for the postulated $[\text{Co}[\text{P}(\text{OCH}_3)_3]_4\text{Na}[(\text{CH}_3\text{O})_3\text{P}]_4\text{Co}^-]$ anion complex is an octahedral solvation of the sodium cation by six oxygen atoms, three from each of the two nominally tetrahedral $[\text{Co}[\text{P}(\text{OCH}_3)_3]_4^-]$ units.

(15) Anal. Calcd for $\text{CoC}_{12}\text{H}_{36}\text{O}_{12}\text{P}_4\text{Na}$: C, 24.92; H, 6.29; P, 21.42; Na, 3.98. Found: C, 25.29; H, 6.21; P, 21.28; Na, 3.47. This salt reacted with allyl bromide in tetrahydrofuran to form $\eta^3\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{OCH}_3)_3]_3$ as established by Hirsekorn and Muettterties⁹ for $\text{KCo}[\text{P}(\text{OCH}_3)_3]_4$ and allyl bromide.

$\text{Co}[\text{P}(\text{OCH}_3)_3]_4$ complex, and the tan monomeric $\text{Co}[\text{P}(\text{OCH}_3)_3]_4$ radical in high yields.¹⁷ The monomeric $\text{Co}[\text{P}(\text{OCH}_3)_3]_4$ species was paramagnetic and exhibited an ESR spectrum (toluene glass at -196 °C) qualitatively interpretable as a $d^9 C_{3v}$ CoP_4 complex (Figure 1). An X-ray crystallographic investigation¹¹ of a crystal of $\text{Co}[\text{P}(\text{OCH}_3)_3]_4$ was attempted, but crystal quality and disorder phenomena precluded a precise, structural analysis.¹⁸ Nevertheless, the crystallographic data were fully consistent with a C_{3v} tetrahedral CoP_4 framework.¹⁹

In the triisopropyl phosphite reaction system, the amalgam reduction generated $[\text{Co}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4^+]$ (the pentakis complex is unstable for steric reasons^{2,3,9}) and $[\text{Co}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4^-]$. We propose that the dimer, $\text{Co}_2[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_8$, is formed by reaction in the ion pair between $[\text{Co}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4^+]$ and $[\text{Co}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4^-]$. The monomer $\text{Co}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4$ presumably is never a high-concentration solution species (and isolable product) because electron transfer at the amalgam interface is very fast to give $[\text{Co}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4^-]$. The reaction sequence leading to the formation of $\text{HCo}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4$, the other major reaction product, has not been established.²¹

Accordingly, in the trimethyl phosphite reaction system, the electron reduction process generated $[\text{Co}[\text{P}(\text{OCH}_3)_3]_4^-]$ and as the cationic complex the very stable trigonal-bipyramidal $[\text{Co}[\text{P}(\text{OCH}_3)_3]_5^+]$ complex and not $[\text{Co}[\text{P}(\text{OCH}_3)_3]_4^+]$, the analogue of the cation produced in the isopropyl phosphite system.^{22a,b} Assemblage of the ionic species generated the primary product $[\text{Co}[\text{P}(\text{OCH}_3)_3]_5^+][\text{Co}[\text{P}(\text{OCH}_3)_3]_4\text{Na}[(\text{CH}_3\text{O})_3\text{P}]_4\text{Co}^-]$. Electron transfer between $[\text{Co}[\text{P}(\text{OCH}_3)_3]_5^+]$ and $[\text{Co}[\text{P}(\text{OCH}_3)_3]_4^-]$ yielded $\text{Co}[\text{P}(\text{OCH}_3)_3]_5$ and $\text{Co}[\text{P}(\text{OCH}_3)_3]_4$, with the former yielding by methyl radical loss^{22c} $\text{Co}[\text{P}(\text{O})(\text{OCH}_3)_2][\text{P}(\text{OCH}_3)_3]_4$ and small amounts of $\text{CH}_3\text{Co}[\text{P}(\text{OCH}_3)_3]_4$. This reaction sequence was independently established in the solution-phase decomposition reaction of $[\text{Co}[\text{P}(\text{OCH}_3)_3]_5^+]\text{Cl}^-$ and $\text{K}^+[\text{Co}[\text{P}(\text{OCH}_3)_3]_4^-]$ as described in footnote 17. The majority of the radical $\text{Co}[\text{P}(\text{OCH}_3)_3]_4$ complex reacted with mercury (vide infra) to form the

(16) Anal. Calcd for $\text{CoC}_{12}\text{H}_{36}\text{O}_{12}\text{P}_4$: C, 25.95; H, 6.55; P, 22.31. Found: C, 26.21; H, 6.48; P, 22.44. ^1H NMR (toluene- d_8 , 35 °C) δ 2.5–0.0 (very br); $^{31}\text{P}\{\text{H}\}$ NMR (toluene- d_8 , -70 °C) no detectable signal. The complex is tan in the solid state and forms colorless solutions in noncoordinating solvents.

(17) A solution of the salt in tetrahydrofuran slowly decomposed (1 day) and on a mole basis produced 1 mol of insoluble $\text{Na}^+[\text{Co}[\text{P}(\text{OCH}_3)_3]_4^-]$ and 1 mol of the reaction products from $[\text{Co}[\text{P}(\text{OCH}_3)_3]_5^+][\text{Co}[\text{P}(\text{OCH}_3)_3]_4^-]$, namely, $\text{Co}[\text{P}(\text{O})(\text{OCH}_3)_2][\text{P}(\text{OCH}_3)_3]_4$ and $\text{Co}[\text{P}(\text{OCH}_3)_3]_4$, with minor amounts of $\text{HCo}[\text{P}(\text{OCH}_3)_3]_4$ and $\text{CH}_3\text{Co}[\text{P}(\text{OCH}_3)_3]_4$. An independent synthesis of $[\text{Co}[\text{P}(\text{OCH}_3)_3]_5^+][\text{Co}[\text{P}(\text{OCH}_3)_3]_4^-]$ from $[\text{Co}[\text{P}(\text{OCH}_3)_3]_5^+]\text{Cl}^-$ and $\text{KCo}[\text{P}(\text{OCH}_3)_3]_4$ showed that this salt decomposed in tetrahydrofuran (1 day) to form $[\text{Co}[\text{P}(\text{OCH}_3)_3]_4^-]$ and $[\text{Co}[\text{P}(\text{O})(\text{OCH}_3)_2][\text{P}(\text{OCH}_3)_3]_4]$ with minor amounts of $\text{HCo}[\text{P}(\text{OCH}_3)_3]_4$ and $\text{CH}_3\text{Co}[\text{P}(\text{OCH}_3)_3]_4$.

(18) To be reported separately.

(19) In the solid state, this monomer possessed rigorous C_3 crystallographic symmetry. Due to the low precision, induced by phosphite ligand disorder, of the crystallographic study, it was not possible to ascertain whether P-Co-P angles and P-Co distances were identical or different within the statistical limits. A static Jahn-Teller distortion is not required for a tetrahedral d^9 complex.

(20) (a) This monomer has been reported: Zecchin, S.; Zotti, G.; Pilloni, G. *Inorg. Chim. Acta* **1973**, *33*, L117. (b) In the $\text{P}(\text{OCH}_3)_3$ system, the radical $\text{Co}[\text{P}(\text{OCH}_3)_3]_4$ had been isolated directly from the reduction reaction by F. J. Hirsekorn (Cornell University, 1974, unpublished data).

(21) Interestingly, a slurry of $\text{NaCo}[\text{P}(\text{OCH}_3)_3]_4$ in tetrahydrofuran slowly reacted with mercury to form $\text{HCo}[\text{P}(\text{OCH}_3)_3]_4$. This reaction could be the source of the small amount of $\text{HCo}[\text{P}(\text{OCH}_3)_3]_4$ produced in the sodium amalgam reduction of cobalt(II) chloride in the presence of $\text{P}(\text{OCH}_3)_3$.

(22) (a) In fact, the $[\text{Co}[\text{P}(\text{OCH}_3)_3]_5^+]$ cationic complex appeared to be formed in the initial reaction between CoCl_2 and excess $\text{P}(\text{OCH}_3)_3$ in tetrahydrofuran solution as established by ^{31}P NMR studies (acetone solution) of such solutions. The anionic species formed in this initial reaction was not definitively characterized but is paramagnetic and presumably is a cobalt(II) species. Verkade and co-workers had shown earlier that cobalt(II) perchlorate and nitrate reacted with $\text{P}(\text{OCH}_3)_3$ to form, among other ionic species, the $[\text{Co}[\text{P}(\text{OCH}_3)_3]_5^+]$ cation: Coskran, K. J.; Huttemann, T. J.; Verkade, J. G. *Adv. Chem. Ser.* **1966**, *62*, 590. (b) $[\text{Co}[\text{P}(\text{OCH}_3)_3]_5^+]$ is itself reduced by sodium amalgam to give $\text{HCo}[\text{P}(\text{OCH}_3)_3]_4$, but in the amalgam reduction of the $\text{CoCl}_2\text{-P}(\text{OCH}_3)_3$ reaction products the anionic cobalt(II) species is first reduced to $[\text{Co}[\text{P}(\text{OCH}_3)_3]_4^-]$ to consume the 2 equiv of reducing agent. (c) A referee suggested the methyl group is lost as a carbonium ion by reaction with a nucleophile, possibly $\text{Co}[\text{P}(\text{OCH}_3)_3]_4^-$, by analogy to the well-established Michaelis-Arbuzov reaction.

mercurial $\text{Hg}[\text{Co}[\text{P}(\text{OCH}_3)_3]_4]_2$. Ostinably,²³ because no substantial quantity of $[\text{Co}[\text{P}(\text{OCH}_3)_3]_4]^+$ was present in this reduction system, no detectable quantity of the dimer $\text{Co}_2[\text{P}(\text{OCH}_3)_3]_8$ was formed.

Aside from the complexity of the trimethyl phosphite based reduction system, the really remarkable features of this chemistry are the isolation of the monomeric and dimeric forms of $\text{Co}[\text{P}(\text{OCH}_3)_3]_4$ and the demonstration of the noninterconvertibility of these two complexes and their relatively low reactivity, as discussed below.

The radical $\text{Co}[\text{P}(\text{OCH}_3)_3]_4$ displayed no detectable degree of dimerization in solution or in the solid state at 25–100 °C nor did the radical abstract hydrogen atoms at 20–70 °C from organic solvents such as tetrahydrofuran or toluene to form the exceedingly stable $\text{HCo}[\text{P}(\text{OCH}_3)_3]_4$ complex. Complementarily, the dimer, $\text{Co}_2[\text{P}(\text{OCH}_3)_3]_8$, gave no evidence of dissociation to the monomer in solution at temperatures below ~70 °C or of hydrogen atom abstraction from solvent at 20–70 °C. Both monomer and dimer in toluene solution very slowly formed $\text{HCo}[\text{P}(\text{OCH}_3)_3]_4$ at 90 °C. Neither the monomer nor the dimer detectably reacted with hydrogen at 20–50 °C (reaction time of 1 week) but they did slowly at 90 °C to form $\text{HCo}[\text{P}(\text{OCH}_3)_3]_4$. Under photolysis at 0 °C, however, both reacted with hydrogen to form $\text{HCo}[\text{P}(\text{OCH}_3)_3]_4$. Photolysis converted both the monomer and the dimer in toluene solution at 0 °C to $\text{Co}[\text{P}(\text{O})(\text{OCH}_3)_2][\text{P}(\text{OCH}_3)_3]_4$. Clearly, this chemistry establishes that the dimer is not formed from the monomer, that the dimer does not thermally dissociate readily to form the monomer, and that the radical monomer does not readily abstract hydrogen atoms from organic solvents. The radical monomer did react slowly with mercury and with sodium amalgam to form $\text{Hg}[\text{Co}[\text{P}(\text{OCH}_3)_3]_4]_2$ and $\text{Na}^+[\text{Co}[\text{P}(\text{OCH}_3)_3]_4]^-$, respectively.²⁴

Much of the chemistry established for the zerovalent phosphite complexes is in sharp contrast to the zerovalent cobalt carbonyl chemistry where the dimer is the only isolable form under normal conditions. Presumably, the stability of $\text{Co}[\text{P}(\text{OCH}_3)_3]_4$ resides in a relative resistance to phosphite dissociation and a large steric barrier to direct dimerization to $\text{Co}_2[\text{P}(\text{OCH}_3)_3]_8$. Carbonyl analogues contrast sharply in their dimerization proclivities. For example, the bimolecular rate constants²⁵ for recombination of $\text{M}(\text{CO})_5$ radicals at 22 °C are 9.5×10^8 and $3.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$, respectively. We are now in the process of examining the thermodynamic and kinetic (reaction mechanistic) character of basic reactions such as ligand substitution in the monomeric $\text{Co}[\text{P}(\text{OCH}_3)_3]_4$ complex and in the dimer.

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Supplementary Material Available: Synthesis details for the amalgam reduction reaction (1 page). Ordering information is given on any current masthead page.

Stereochemical Consequence of the Interaction of Alkylaluminums with Titanacyclobutanes and Its Relationship to the Olefin Metathesis Reaction

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Lewis acids are necessary cocatalysts in many olefin metathesis^{1,2} and Ziegler–Natta polymerization^{3,4} systems. Many of these catalyst systems are highly stereospecific but become less so on increasing the concentration of the Lewis acid cocatalyst.² We describe here the stereochemical result of the interaction of a Lewis acid, dimethylaluminum chloride, with a bis(η^5 -cyclopentadienyl)titanacyclobutane, a well-defined olefin metathesis catalyst.⁵

Compound I⁵ (Chart I) is smoothly converted to II⁶ and 3,3-dimethyl-1-butene (Scheme I) with dimethylaluminum chloride. The reactions were followed by ^1H or ^2H NMR spectroscopy.¹⁸ The reaction proceeds with second-order kinetics, first order in I and Me_2AlCl ($k_2 = (5.8 \pm 1.7) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 294 K). A plot of $\ln(k/T)$ vs. $1/T$ yields $\Delta G^\ddagger_{294} = 20 \pm 1 \text{ kcal/mol}^{-1}$, and $\Delta S^\ddagger = -38 \pm 1 \text{ eu}$. A small secondary isotope effect was observed ($k_{\text{H}}/k_{\text{D}} = 1.18 \pm 0.2$) in the reaction of I- d_2 ⁷ and Me_2AlCl , producing 3,3-dimethyl-1-butene-1,1- d_2 and II- d_2 in the ratio $1.40 \pm 0.03:1$. Scheme I shows a reasonable mechanism for this reaction and, therefore, the cocatalyzed route for metathesis.⁸

As part of a study of the stereochemistry of the metathesis reaction catalyzed by *trans*-I- d_1 , a surprising result was observed. During reaction of *trans*-I- d_1 with Me_2AlCl , ^2H NMR spectroscopy at 77 MHz indicated that the stereochemistry of the α -carbon of the metallacycle was rapidly (only a few seconds are required) and completely scrambled, giving equal amounts of *cis*- and *trans*-I- d_1 before cleavage to II and II- d_1 . We have since found that *trans*-I- d_1 is rapidly and catalytically isomerized by less than 0.1 equiv of Me_2AlCl at room temperature.

Initially, we considered that a possible mechanism for the isomerization involved a reversible β -H abstraction by Me_2AlCl to produce a titanocene allyl cation (Scheme II). Rapid rotation of a C–C bond via an η^3 – η^1 allyl rearrangement in the cation

(1) For leading references, see: Katz, T. J.; Lee, S. J.; Nair, M.; Savage, E. B. *J. Am. Chem. Soc.* **1980**, *102*, 7940.

(2) Gunther, P.; Pampus, G.; Haas, F.; Marwede, G.; Nützel, K.; Oberkirch, W.; Schön, N.; Witte, J. *Angew. Makromol. Chem.* **1970**, *14*, 87.

(3) See: Boor, Jr., J. "Ziegler–Natta Catalysts and Polymerizations"; Academic Press: New York, 1979; pp 118–124 and references therein.

(4) Pino, P.; Mulhaupt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 857 and references therein.

(5) Lee, J. B.; Howard, T. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4515.

(6) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611.

(7) Compounds I, I- d_2 , and *trans*-I- d_1 were prepared as previously described (ref 5) from II, the corresponding olefin, and 4-dimethylaminopyridine (DMAP). I- d_2 was prepared from II- d_2 which had been prepared by reaction of Cp_2TiCl_2 with 2 equiv of AlMe_3 - d_9 . I-2,3- d_2 was prepared by exchange of $\text{Cp}_2\text{TiCH}_2\text{CMe}_2\text{CH}_2$ with *cis*-3,3-dimethyl-1-butene-1,2- d_2 .

(8) Tebbe has shown that II will catalyze the metathesis of terminal olefins: Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074. Klabunde, U.; Tebbe, F. N.; Parshall, G. W.; Harlow, R. L. *J. Mol. Catal.* **1980**, *8*, 37. This metathesis is slow, even at 51 °C. From this work, we infer the existence of the olefin II complex depicted in Scheme I.

(23) We infer that dimers are formed only by electron transfer between $[\text{Co}[\text{P}(\text{OR})_3]_4]^+$ and $[\text{Co}[\text{P}(\text{OR})_3]_4]^-$. The only established synthesis of $\text{Co}_2[\text{P}(\text{OCH}_3)_3]_8$ is from $\text{K}^+[\text{Co}[\text{P}(\text{OCH}_3)_3]_4]^-$ and $(\text{CH}_3)_3\text{GeCl}$.⁵ We assume that in this reaction, electron transfer yields the cationic $[\text{Co}[\text{P}(\text{OCH}_3)_3]_4]^+$ species, which then reacts with $[\text{Co}[\text{P}(\text{OCH}_3)_3]_4]^-$ to form the dimer. Consistent with this proposal, the germanium-containing product of the reaction was $\text{Ge}_2(\text{CH}_3)_6$.

(24) Explicitly, the monomer was oxidized by silver ion to give $\text{Co}[\text{P}(\text{OCH}_3)_3]_5^+$. The monomer also reacted rapidly with oxygen. An oxygen complex, deep purple, formed at –78 °C. Thermal reactivity of the complex was high, as evidenced by the irreversible color changes to dark green at –10 °C and to blue at 15 °C. Addition of 2 more equivalents of oxygen at 20 °C discharged the blue color within minutes, and brown solids separated.

(25) Wegman, R. W.; Olsen, R. J.; Gard, D. R.; Faulkner, L. R.; Brown, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 6089.