Supplementary Material Available: Tables of atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, H atom coordinates, and isotropic thermal parameters (5 pages); a table of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

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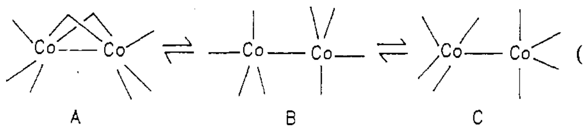
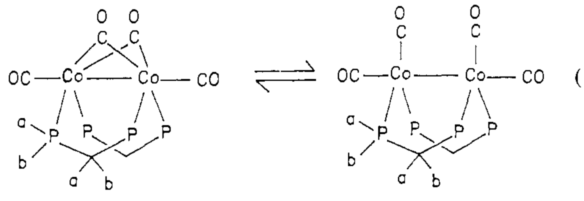
Thermodynamics and Dynamics of the Equilibrium between Carbonyl-Bridged and Nonbridged Isomers of $[Co_2(CO)_4(\mu\text{-}R_2PCH_2PR_2)_2]$ (R = Me, Ph)

The complex $[Co_2(CO)_8]$ and its phosphine-substituted derivatives are important in catalysis, and the interconversion between its three structural forms, A–C, has been studied in detail (eq 1).[1-4]



(1)

However, the interconversions are too rapid even at −150 °C to allow a study of the dynamics by ^{13}C NMR spectroscopy, and so little is known about the fluxionality.[3] The situation is similar in those phosphine-substituted derivatives that have been studied previously, including $[Co_2(CO)_4(\mu\text{-}CO)_2(\mu\text{-}dppm)]$.[5] It is therefore of interest that the complexes $[Co_2(CO)_4(\mu\text{-}dppm)_2]$ (4)[6,7] and $[Co_2(CO)_4(\mu\text{-}dmpm)_2]$ (5)[8] (dppm = $Ph_2PCH_2PPh_2$, dmpm = $Me_2PCH_2PMe_2$) can exist in either bridged or unbridged forms (eq 2) and that the dynamics of the reaction can be studied by NMR spectroscopy.



(2)

4a, PP = dppm
5a, PP = dmpm

4b, PP = dppm
5b, PP = dmpm

The equilibria were most readily monitored by variable temperature FTIR spectroscopy (Figure 1, supplementary material). This showed clearly that the unbridged isomer **4b** or **5b** was favored at higher temperatures and the bridged form **4a** or **5a** was favored at lower temperatures.[9] The equilibrium constants were determined over a range of temperatures from 190 to 301 K, and the thermodynamic data were then determined (Table I).[10] In each case, the enthalpy term strongly favors the carbonyl-bridged form while the entropy term strongly favors the unbridged form. The effect is much greater than in $[Co_2(CO)_8]$[1-4] as can be seen from the data in Table I.

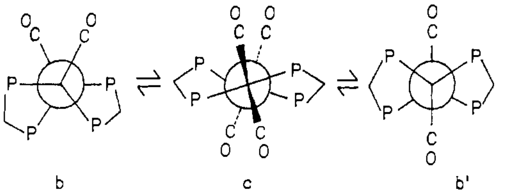
Table I. Thermodynamic and Kinetic Data for the Carbonyl-Bridged ⇌ Nonbridged Isomerism

complex	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	ratio b:nb[c]		$\Delta G^\ddagger$/kJ mol^{-1}
			298 K	190 K	
$[Co_2(CO)_8]$[a]	+5.6	+21	44:56	74:26	27
$[Co_2(CO)_4(\mu\text{-}dppm)_2]$[b]	+22.1 (1.5)	+102 (8)	3:97	85:15	41.5 (1.0)
$[Co_2(CO)_4(\mu\text{-}dmpm)_2]$[b]	+26.3 (2.1)	+107 (13)	9:91	98:2	47 (1)

[a] For A ⇌ B in pentane or hexane (eq 1) from ref 2 and 3. The value for $\Delta G^\ddagger$ was obtained in a hexane matrix and assumes no matrix contribution. This is reasonable in light of recent work.[13] [b] For a ⇔ b in CH_2Cl_2 (eq 2). [c] b = CO bridged form, and nb = nonbridged form; these ratios are the calculated values at 298 or 190 K based on the ΔH and ΔS values given.

The fluxionality of **4** and **5** was studied by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies, with the ^{13}C NMR spectra obtained on ^{13}CO-enriched samples.[11] For example, the ^{13}C NMR spectrum of **4** at low temperature gave two carbonyl resonances due to **4a** and one due to **4b**, and the resonances coalesced to give a singlet at room temperature (Figure 2, supplementary material). Similarly, the ^{1}H NMR spectrum due to the CH_2P_2 protons gave a singlet at room temperature but gave two broad resonances for **4a**, due to the nonequivalent protons CH^aH^b, and one resonance for **4b** at low temperature. A single ^{31}P resonance was observed at room temperature but two resonances, one for each of **4a** and **4b**, were observed at low temperatures (Figure 2). Very similar spectroscopic features were observed for complex **5**, and this complex also gave two resonances due to the nonequivalent Me^aP and Me^bP groups of **5a** at low temperature, but gave a single resonance at room temperature.

It is clear that **4b** or **5b**, in the static form established crystallographically for the solid state of **4b**, should also give two carbonyl resonances and two $CH^aH^bP_2$ resonances, but this nonequivalence was not observed. Furthermore, the reaction of eq 2 does not, of itself, lead to equivalence of the carbonyl groups or the CH^aH^b protons of **4a** or **5a**. Thus, a second form of fluxionality with a much lower activation energy must occur within the nonbridged form **4b** or **5b**. The mechanism of eq 3 (showing



(3)

Newman projections along the Co–Co bond), involving reversible reaction of b ⇌ c is most reasonable,[1-4] since c is analogous to

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[1] Bor, G.; Dietler, U. K.; Noack, K. *J. Chem. Soc., Chem. Commun.* **1976**, 914.
[2] Noack, K. *Helv. Chim. Acta* **1964**, *47*, 1064.
[3] Lichtenberger, D. L.; Brown, T. L. *Inorg. Chem.* **1978**, *17*, 1381. Sweany, R. L.; Brown, T. L. *Inorg. Chem.* **1977**, *16*, 415.
[4] Onaka, S.; Shriver, D. F. *Inorg. Chem.* **1976**, *15*, 915.
[5] Lisic, E. C.; Hanson, B. E. *Inorg. Chem.* **1986**, *25*, 812.
[6] Elliot, D. J.; Holah, D. G.; Hughes, A. N. *Inorg. Chim. Acta* **1988**, *142*, 195.
[7] The complexes **4a** and **4b** have been characterized by X-ray structure determinations. Elliot, D. J.; Holah, D. G.; Hughes, A. N.; Magnuson, V. R.; Moser, I. To be submitted for publication.
[8] The complex **5** was prepared by reaction of cobalt(II) bromide with $Na[BH_4]$ in the presence of CO and the diphosphine ligand.
[9] FTIR data [ν(CO)/cm^{-1} in CH_2Cl_2]: **4a**, 1951, 1924, 1765 sh, 1753; **4b**, 1972, 1953, 1921; **5a**, 1945, 1916, 1735 sh, 1716; **5b**, 1953, 1920, 1893. The observation of nearly isosbestic points in each case indicates that only two isomers are present.
[10] In each case data were measured at two wavelengths, and the data given are the mean values determined.
[11] NMR data at low temperature in CD_2Cl_2 are as follows. **4a**: ^{1}H, −90 °C, δ = 2.84, 3.71 (CH^aH^b); ^{13}C, −70 °C, δ = 206.0 (terminal CO), 244.3 (μ-CO); ^{31}P, −70 °C, δ = 44.8. **4b**: ^{1}H, −90 °C, δ = 3.89 (CH_2); ^{13}C, −70 °C, δ = 213.95 (CO); ^{31}P, −70 °C, δ = 37.4. **5a**: ^{1}H, −92 °C, 1.93, 2.75 (CH^aH^b), 1.50 (MeP); ^{13}C, −82 °C, δ = 203.5 (terminal CO), 265.5 (μ-CO), δ = 19.5, 19.0 (MeP); ^{31}P, −62 °C, δ = 29.85. **5b**: ^{1}H, −90 °C, δ = 2.19 (CH_2), 1.34 (MeP); ^{13}C, not resolved; ^{31}P, −62 °C, δ = 19.3. The chemical shifts and peak widths were, in many cases, temperature dependent, at least partly due to the quadrupole of cobalt (see Figure 2).

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the proposed structure of the third isomer of $[Co_2(CO)_8]$, C (eq 1), and has equivalent carbonyl and CH_2 groups. There is no necessity for formation of the other likely isomer of eq 3, b′, which could form via isomer c.

The activation energies, ΔG^*, for exchange of **4a** or **5a** with **4b** or **5b** and for making equivalent the nonequivalent carbonyl, Me_2P, or $C\mathit{H}_2$ groups of **4a** or **5a**, were identical within ±1 kJ mol^{-1} for a given complex and the data are given in Table I.[12] These data show clearly that the reaction of eq 2 is rate determining and that carbonyl exchange then occurs rapidly by way of eq 3. Furthermore, there is a very good correlation of the ΔH° and ΔG^* values for the bridged $\rightleftharpoons$ nonbridged reactions as shown in Table I. This relationship is expected[12] but has not previously been demonstrated for the important cobalt carbonyl dimers.

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Supplementary Material Available: Figure 1 (variable-temperature FTIR spectra of $[Co_2(CO)_4(\mu\text{-dmpm})_2]$ in CH_2Cl_2 (the arrows indicate growth of peaks due to **5a** at lower temperature) and the resulting plot of ln K vs $1/T$, where K is the equilibrium constant for eq 2) and Figure 2 (variable-temperature ^{13}C NMR (75-MHz) and ^{31}P NMR (121-MHz) spectra for $[Co_2(CO)_4(\mu\text{-dppm})_2]$) (2 pages). Ordering information is given on any current masthead page.

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[12] The ΔG^* values were estimated by using the Eyring equation and were unchanged over the temperature range 213–243 K for **4** and 233–275 K for **5**. This suggests that ΔS^* is small and hence $\Delta G^* \sim \Delta H^*$. The entropy term favors **4b** or **5b** because of the greater mobility compared to **4a** or **5a**, but libration about the Co–Co bond is not expected to be possible until the μ-CO bonds in the bridged isomer are *completely* broken, and so the entropy of activation term is not expected to be an important contributor to ΔG^*. If it were otherwise, the observed correlation of ΔH° and ΔG^* would not be expected. The entropy term is probably also responsible for the relative instability of isomer b′ (eq 3). Molecular models indicate that b′ is strain free but the conformation is rigid, whereas in b libration about the Co–Co bond is possible.

[13] Hill, R. H.; Wrighton, M. S. *Organometallics* **1985**, *3*, 413.

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Synthesis of Tris(triphenylsiloxy)yttrium and Derivatives: Crystal Structure of $[Y(OSiPh_3)_3(THF)_3]\cdot THF$

One approach to the incorporation of yttrium into mixed-metal, solid-state materials is envisioned as proceeding through *molecular* precursors that are ligand-bridged aggregates of the sort $Y_aM_bX_n$ (M = any other metal; X = any bridging ligand).[1] Since an oxide lattice is frequently desired, the ligand complement to the molecular aggregate must be chosen, in part, for its ability to be subsequently removed by hydrolysis with concomitant introduction of oxo groups. In this regard yttrium alkoxides are relevant starting reagents for the assembly of preceramic aggregates, although they remain poorly characterized.[2] Initial efforts in this laboratory at the preparation of tri-*tert*-butoxyyttrium complexes invariably led to the obtention of white, poorly soluble materials that could not be characterized further. Because heterolytic cleavage of the carbon–oxygen bond leading to yttrium oxides and organic products derived from the *tert*-butyl carbocation might be a facile decomposition pathway,[3] attention focused on yttrium silyloxides because of the strength of the Si–O linkage and the unfavorability of silyl cation formation. We now wish to report the synthesis of $[Y(OSiPh_3)_3]_n$ (**1**) along with two monomeric Lewis base adducts, *fac*-$[Y(OSiPh_3)_3(THF)_3]\cdot THF$ (**2**) and *fac*-$[Y(OSiPh_3)_3(py)_3]$ (**3**).

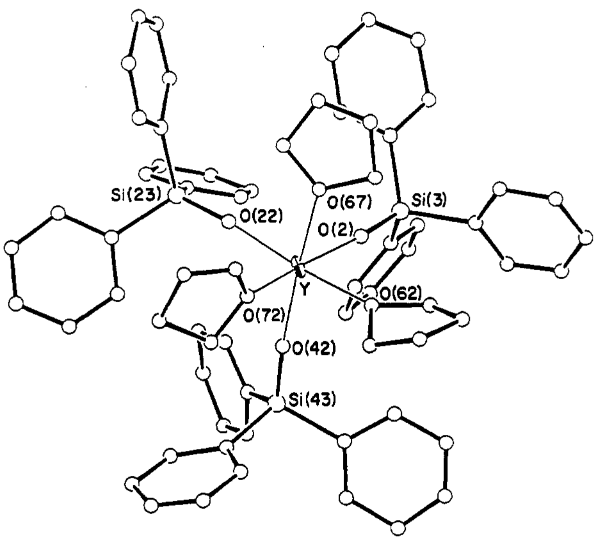

Figure 1. ORTEP drawing of $Y(OSiPh_3)_3(THF)_3$, omitting hydrogens. Selected structural parameters: Y–O2 = 2.136 (17) Å, Y–O22 = 2.118 (18) Å, Y–O42 = 2.138 (18) Å, Y–O62 = 2.406 (21) Å, Y–O67 = 2.462 (21) Å, Y–O72 = 2.374 (20) Å, Si–O = 1.554 (19)–1.597 (20) Å. Angles: Y–O–Si = 168.5 (12)–174.4 (11)°, (Si)O–Y–O(Si) = 100.8 (7)–102.3 (7)°, $(C_4H_8)O\text{–}Y\text{–}O(C_4H_8)$ = 79.6 (7)–82.2 (7)°. Unlabeled atoms are carbon atoms.

Tris(triphenylsilyloxy)yttrium (**1**), formed from the reaction of $Y[N(SiMe_3)_2]_3$[4] with 3 equiv of Ph_3SiOH in toluene (eq 1), was

$$Y[N(SiMe_3)_2]_3 + 3Ph_3SiOH \xrightarrow[0^\circ C]{\text{toluene}} [Y(OSiPh_3)_3]_n + 3HN(SiMe_3)_2 \quad (1)$$

isolated as a colorless, feather-like solid.[5] The hydrogen-1 and carbon-13 NMR spectra of **1** showed only broad, complex resonances in the phenyl region, consistent with the formulation of this compound as an aggregate presumably involving bridging

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[1] Hubert-Pfalzgraf, L. G. *New J. Chem.* **1987**, *11*, 663.

[2] (a) Hart, F. A. Scandium, Yttrium and the Lanthanides. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 3, Chapter 39, pp 1065–66. (b) Bradley, D. C.; Mehrotra, C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: New York, 1978; p 74.

[3] Lapointe, R. E.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics* **1985**, *4*, 1810.

[4] Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021.

[5] $[Y(OSiPh_3)]_n$ (**1**). IR (Nujol): no ν(O–H); ν(C–H) 3030 cm^{-1}; other bands 1100 (s), 695 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.5–6.5 (br mult). ^{13}C NMR (CD_2Cl_2): a complex set of resonances between δ 135.4 and 127.6. Anal. Calcd for $C_{54}H_{45}O_3Si_3Y$: C, 70.87; H, 4.97. Found: C, 69.99; H, 4.89. $[Y(OSiPh_3)_3(THF)_3]\cdot THF$ (**2**). IR (Nujol): no ν(O–H); ν(C–H) 3040, 3020 cm^{-1}; aromatic overtones 1945, 1875, 1810, 1760 cm^{-1}; other bands 1100 (vs), 695 (s) cm^{-1}. ^1H NMR (THF-d_8): δ 7.65 (d, 6.7 Hz, 18 H, ortho H), 7.09 (t, 7.5 Hz, 9 H, para H), 6.94 (~t, 7.1 Hz, 18 H, meta H), 3.58 (m, 16 H, THF), 1.74 (m, 16 H, THF). ^{13}C NMR (THF-d_8): δ 142.4 (ipso), 136.4 (ortho), 128.7 (para), 127.8 (meta), 68.2 (THF), 26.4 (THF). Anal. Calcd for $C_{70}H_{77}O_7Si_3Y$: C, 69.85; H, 6.46. Found: C, 66.88; H, 6.15. Crystal data (−157 °C): monoclinic, space group $P2_1$, a = 14.530 (7) Å, b = 16.407 (8) Å, c = 14.534 (8) Å, β = 114.32 (2)°, V = 3157.21 $Å^3$, Z = 2. Refinement of 1926 reflections with $|F^2| > 3\sigma(F^2)$ converged with final residuals R = 0.0841 and R' = 0.0790. $[Y(OSiPh_3)_3(py)_3]$ (**3**). IR (Nujol): no ν(O–H); ν(C–H) 3040, 3020 cm^{-1}; ν(C–N) 1590 cm^{-1}; other bands 1100 (vs), 695 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.35 (br s, 6 H, py α), 7.42 (br m, 3 H, py δ), 7.37 (d, 7.0 Hz, 18 H, ortho H), 7.10 (t, 7.4 Hz, 9 H, para H), 6.93 (~t, 7.4 Hz, 18 H, meta H), 6.74 (br s, 6 H, py β). ^{13}C NMR ($CDCl_3$): δ 149.9 (py α), 140.8 (ipso), 137.6 (py β), 135.2 (ortho), 128.1 (meta), 127.1 (para), 123.8 (py β). Anal. Calcd for $C_{69}H_{60}N_3O_3Si_3Y$: C, 71.90; H, 5.26; N, 3.65. Found: C, 71.08; H, 5.60; N, 3.44.

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