hanced reactivities of odd-electron organometallic fragments.

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Registry No. 1, 88864-12-4; 1-d_{10}, 141439-21-6; 2, 141439-19-2; A, 141439-24-9; $Pt(Ch_2CMe_2Ph)_2(cod)$, 88864-93-1; $ClCH_2CMe_2Ph$, 515-40-2; $PtCl_2(cod)$, 12080-32-9; $Pt(CH_2CMe_2C_6D_5)_2(cod)$, 118334-63-7; $PtCl(CH_2CMe_2Ph)(cod)$, 141439-20-5; $PtCl(CH_2CMe_2Ph)(dppe)$, 141439-22-7; $Pt(CH_2Ph)(CH_2CMe_2Ph)(cod)$, 141439-23-8; $ClCMe_2CH_2Ph$, 1754-74-1; $Mg(CH_2CMe_2Ph)Cl$, 35293-35-7; $Pt(CH_2CMe_2Ph)(CMe_2CH_2Ph)(cod)$, 141439-25-0; $Pt(PhCH{=}CMe_2)(dppe)$, 141439-26-1; $PhCH{=}CMe_2$, 768-49-0; $Pt(C_2H_4)(dppe)$, 83571-74-8; $Pt(CH_2CMe_2Ph)(2\text{-}C_6H_4CMe_3)(dppe)$, 141439-27-2; D_2, 7782-39-0.

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Preparation, Solution Structures, and Nucleophilic Reactions of Chiral, Bimetallic Complexes: $[(\mu\text{-}\eta^2,\eta^3\text{-propargylium})Co_2(CO)_5P(C_6H_5)_3]BF_4$

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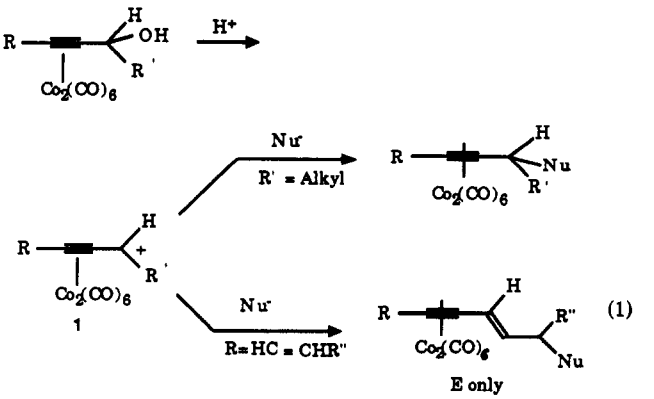
Chiral complexes of the type $[(\mu\text{-}\eta^2,\eta^3\text{-}R^1C_2CR^2R^3)Co_2(CO)_5PPh_3]BF_4$ (3) have been synthesized and characterized. Formation of 3 via protonation of the corresponding alcohol complexes $[(\mu\text{-}\eta^2,\eta^2\text{-}R^1C_2C(OH)R^2R^3)Co_2(CO)_5PPh_3$ (2) proceeds readily. Where diastereomeric alcohol complexes are available (smaller R^2 substituents), protonation of either isomer gives the same initial mixture of cations with good stereoselectivity; single isomeric cations are obtained where R^2 = ^{i}Pr or ^{t}Bu. The preferred (or exclusive) isomer has an anti geometry on the basis of difference NOE NMR experiments with the $-Co(CO)_2PPh_3^+$ unit η^3-bonded. The isomeric mixtures slowly equilibrate ($\Delta G^\ddagger$ = 17–20 kcal/mol) in acetone solution to ca. a 1:1 anti/syn ratio. Spin saturation transfer experiments failed to detect the intervention of an enantiomerization process. Quenching those complexes having smaller R^2 groups with oxygen-centered nucleophiles yields primarily the less stable (1*S**,2*S**,3*R**) diastereomers, whereas the complexes 3 with R^2 = ^{i}Pr or ^{t}Bu are quenched to re-form the original (1*R**,2*S**,3*R**) isomer. Carbon nucleophiles have not been successfully added. Structural and mechanistic models are proposed to explain these results.

Introduction

Transition metal-directed asymmetric synthesis has been an important goal of organic and organometallic chemists for several years. Some impressive success has been achieved using monometallic complexes in both stoichiometric[1] and catalytic[2] reactions. On the other hand, success with polynuclear systems has been negligible, in part because of the limited access to and stereochemical instability of such complexes[3] and also because of the paucity of synthetically useful organic transformation of metal clusters.[4]

One of the few classes of polynuclear complexes with demonstrated synthetic organic utility is the $(\mu\text{-}\eta^2,\eta^2\text{-}$alkyne$)Co_2(CO)_6$ system. Two aspects of the chemistry of these complexes have received the most attention synthetically. Their thermal cyclization reactions with olefins (Pauson–Khand reaction[5]) have been widely used as a route to substituted cyclopentenone derivatives. Additionally, the propargylium complexes 1 react as electrophiles with a variety of carbon nucleophiles to provide propargylated organics (following demetalation) with complete regioselectivity (eq 1[6]). Recently, we have been



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(1) Reviews: Blystone, S. *Chem. Rev.* **1989**, *89*, 1663; *Tetrahedron* **1985**, *41*, entire issue No. 24. Collman, J. P.; Hegedus, L.; Norton, J. R.; Finke, R. G. In *Principles and Application of Organometallic Chemistry*; University Science Books: Mill Valley, CA, 1988; pp 775–778. Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 151.

(2) Reviews: Kagan, H. C.; Frian, J. C. New Approaches in Asymmetric Synthesis. *Top. Stereochem.* **1977**, *10*. 175. Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106. Brunner, H. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Ed.; Wiley and Sons: New York, 1990; Vol. 5, Chapter 4. Inoue, S. I.; Takaya, H.; Tani, K.; Otsuka, S.; Sato, T.; Noyori, R. *J. Am. Chem. Soc.* **1990**, *112*, 4897 and references therein. Ojima, I.; Clos, N.; Bastos, C. *Tetrahedron* **1989**, *45*, 6901.

(3) (a) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169. (b) D'Agostino, M. F.; Frampton, C. S.; McGlinchey, M. J. *Organometallics* **1990**, *9*, 2972. McGlinchey, M. J.; Mlekuz, M.; Bougeard, P.; Sayer, B. G.; Marinetti, A.; Saillard, J.-Y.; Jaouen, G. *Can. J. Chem.* **1983**, *61*, 1319.

(4) (a) Suss-Fink, G.; Newmann, F. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Ed.; Wiley and Sons: New York, 1990, Vol. 5, Chapter 7. (b) Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97.

(5) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Forman, M. I. *J. Chem. Soc., Perkin Trans. 1* **1973**, 97. Schore, N. E.; Croudace, M. C. *J. Org. Chem.* **1981**, *46*, 5436. Exon, C.; Magnus, P. *J. Am. Chem. Soc.* **1983**, *105*, 2477.

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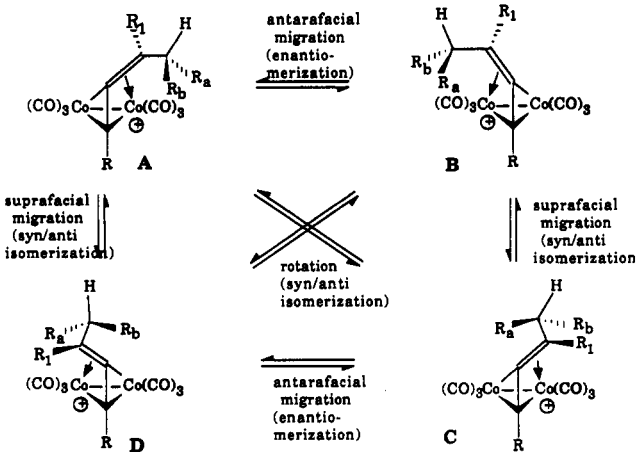


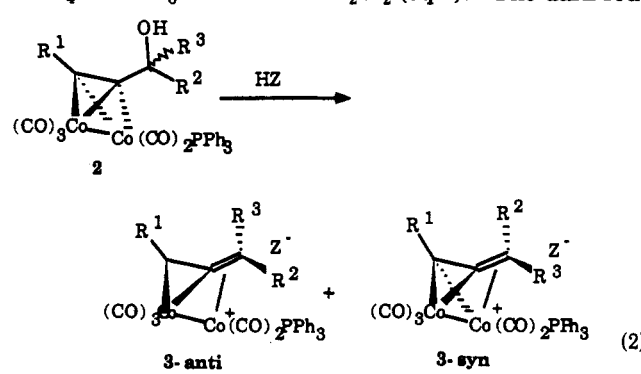
Figure 1. Isomerization processes for (propargylium)$Co_2(CO)_6^+$ complexes 1.

interested in the development of strategies for the relative and absolute stereocontrol in these latter reactions.[6c-e,7] Of primary interest is the modification of these complexes in such a way as to introduce and to maintain chirality. Rational approaches to this objective require a thorough knowledge of the structural features of the cations 1. This requirement has been difficult to satisfy because of our lack of success in obtaining X-ray-quality crystals and because of the dynamic structural behavior of 1 in solution. Previous NMR studies in this laboratory[8] and Schreiber's[6g] have shown that these cations exist as unsymmetrical structures; Schreiber suggested "bent" structures A–D (Figure 1) as the most stable forms for the cations on the the basis of the available spectroscopic data and theoretical studies of the isolobal $(CO)_9Co_3CCHR^+$ complexes.[4b,9] Lending further indirect support to the proposed bent, unsymmetrical structures for 1 is a recent report by Curtis and co-workers describing the isolobal $[Cp_2Mo_2(HC_2CH_2)(CO)_4]BF_4$[10] including its X-ray structure which features an unsymmetrical structure in which the bent propargyl ligand adopts an η^2,η^3-coordination mode. Furthermore, ^1H NMR spectral data for the Mo_2 and Co_2 complexes are strikingly similar. Importantly, the cations 1 exhibit dynamic stereochemical behavior, interconverting via a series of facial migrations leading to enantiomerization and syn/anti isomerizations (Figure 1). In general, the major isomer has the syn geometry (CHR_2 relative to R), as shown by NOE effects in the ^1H NMR spectrum. The lower energy pathway (enantiomerization) was found to have a barrier of 10.5 kcal/mol. At higher temperatures a second process, ascribed to syn/anti interconversion (A → C and B → D) was observed with a corresponding ΔG^* of 12.9 kcal/mol. The diastereomerization energy barriers have been found to depend considerably on the degree of substitution at C1, decreasing in the order 1° > 2° > 3°. These dynamic isomerization processes were found to be fast relative to some reactions with nucleophiles,[6g] limiting opportunities for enantioselective transformations. Nonetheless, high syn diastereoselectivities have been obtained via reactions of silylenol ethers with rapidly equilibrating chiral (or prochiral) cations.[6f,g]

We have considered several possible methods of asymmetric induction utilizing derivatives of the propargylium complexes 1, including the use of homochiral propargyl alcohols, chiral nucleophiles, or a chiral cluster core as a chiral auxiliary. This manuscript describes the second phase of our investigations of the last approach. In the first phase we synthesized and characterized a series of chiral clusters of the type $[RC_2CH(OH)R^1]Co_2(CO)_5(PPh_3)$ (2[7]). The diastereomeric complexes 2 are typically formed with significant stereoselectivity, are chromatographically separable, and are relatively stable to air and water. Although the compounds do slowly isomerize in solution, the isomerization half-life (~350–400 h/20 °C) is considerably longer than that of many other chiral clusters[3] and is significantly longer than anticipated for subsequent reactions of the derived cations with nucleophiles. One can envision extension to chiral, nonracemic derivatives using either readily available optically active propargyl alcohols[11] or phosphines. These initial observations offered promise for the development of a practical synthetic methodology for stereoselective coupling reactions using the electrophilic chiral cations $[(R^1C_2CR^2R^3)Co_2(CO)_5(Ph_3P)]Z$ (3) derived from 2.

Results

Synthesis and Characterization. Preparation of the cationic complexes $[(R^1C_2CR^2R^3)Co_2(CO)_5(Ph_3P)]Z$ (3, Z = BF_4^-, PF_6^-) is conveniently accomplished by treatment of the alcohol derivatives 2 with 3–5 equiv of anhydrous HBF_4 or HPF_6 in ether or CH_2Cl_2 (eq 2). The dark red,



(2)

rather air-stable powders are obtained in virtually quantitative yield (>95%) and high purity (except for traces of trapped solvent) and have been characterized spectroscopically (Table I). Attempts to obtain X-ray-quality crystals of 3 by low-temperature recrystallization from a variety of solvents have been uniformly unsuccessful to date, often resulting in slow decomposition to $(Ph_3P)_2Co(CO)_3BF_4$.[12]

Comparison of the IR and NMR data for 3 in Table I with corresponding data for the precursor alcohols 2[7] and

(6) (a) Review: Nicholas, K. M. *Acc. Chem. Res.* **1986**, *20*, 207. (b) Stuart, J. G.; Nicholas, K. M. *Synthesis* **1989**, *6*, 454. (c) Montana, A. M.; Nicholas, K. M. *J. Org. Chem.* **1990**, *55*, 1569. (d) Tester, R.; Varghese, V.; Montana, A. M.; Khan, M.; Nicholas, K. M. *J. Org. Chem.* **1990**, *55*, 186. (e) Ju, J.; Reddy, B. R.; Khan, M.; Nicholas, K. M. *J. Org. Chem.* **1989**, *54*, 5426. (f) Schreiber, S. L.; Sammakia, T.; Crowe, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 3128. (g) Schreiber, S. L.; Klimas, M. T.; Sammakia, S. *J. Am. Chem. Soc.* **1987**, *109*, 5749. (h) Marshall, J. M.; Gung, W. Y. *Tetrahedron Lett.* **1989**, *30*, 2183. (i) Magnus, P.; Lewis, R. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 6921. (j) Smit, W. A.; Schegolev, A. A.; Gybin, A. S.; Mikaelin, G. S.; Caple, R. *Synthesis* **1984**, 887. (k) Nicholas, K. M.; Mulvaney, M.; Bayer, M. *J. Am. Chem. Soc.* **1980**, *102*, 2508.

(7) Bradley, D. H.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1989**, *8*, 554.

(8) (a) Connor, R.; Nicholas, K. M. *J. Organomet. Chem.* **1977**, *125*, C45. (b) Padmanabhan, S.; Nicholas, K. M. *J. Organomet. Chem.* **1983**, *268*, C23.

(9) (a) Hoffman, D. M.; Hoffman, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858. (b) Pepermans, H.; Hoogzand, C.; Geerlings, P. *J. Organomet. Chem.* **1986**, *306*, 395.

(10) Meyer, A.; McCabe, D. J.; Curtis, M. D. *Organometallics* **1987**, *6*, 1491.

(11) Midland, M. M. *Chem. Rev.* **1989**, *89*, 1553. Burgess, K.; Jennings, L. D. *J. Am. Chem. Soc.* **1991**, *113*, 6129 and references therein.

(12) Schumann, H. *J. Organomet. Chem.* **1985**, *290*, C34.

Table I. Yields and Selected Spectroscopic Data for $[(R^1C_2CR^2R^3)Co_2(CO)_5PPh_3]BF_4$ (3)

compd	R^1	R^2	R^3	yield, %	IR (ν_{CO})[a]	^{1}H NMR[b,c]	^{13}C NMR[d]	^{31}P NMR[e]
3a	H	H	H	97	2060, 2015 (sh), 2050, 1990, 1980 (sh)	3.39, 3.37 (2 d, J = 14 Hz) (3.35, 3.33, J = 12 Hz)	88.2 (63.2)	57.2 (51.1)
3b	H	Me	H	96	2075, 2010, 2000, 1995	4.10, 3.88 (2 q, J = 8 Hz) (3.80, 3.83, dt, J = 5.4, 7 Hz)	88.4 (73.3)	53.6, 55.9 (54.0, 54.1)
3c	H	Ph	H	95	2085, 2005, 1995	7.25 (s) (4.89, 5.0)	88.5 (73.6)	53.3 (54.5, 53.4)
3d	H	Pr^i	H	97	2060, 2050, 2010, 2005	6.72 (d, J = 10 Hz) (2.9, dd, J = 3, 7 Hz)	88.8 *73.4)	53.8 (54.0)
3e	H	Bu^t	H	99	2060, 2010, 1990, 1980 (sh)	7.21 (s) (3.4, d, J = 7 Hz)	78.3 (73.6)	53.6 (54.0)
3f	Me	Me	H	96	2075, 2020, 2005, 1990	6.24, 5.95 (both q, J = 5 Hz) (4.0, dq, J = 3, 7 Hz)	84.6 (71.8)	55.7, 57.3 (54.0)
3g	Ph	Me	H	97	2080, 2025 (sh), 2010, 1990	4.18, 4.05 (both q, J = 6 Hz) (4.02, 4.06, q, J = 6 Hz)	99.0 (67.9)	53.2, 52.1 (50.0)
3h	Ph	Pr^i	H	96	2070, 2025, 2005, 1995 (sh)	6.93 (d, J = 10 Hz) (3.2, m)	110.4 (75.3)	53.1 (49.1)
3i	H	Me	Me	96	2075, 2060, 2005, 1995	1.25, 1.19 (s)[f], (1.18, 0.98, s)	89.1 (67.7, 67.9)	53.2 (52.5)

[a] In THF, cm^{-1}. [b] Cations in acetone-d_6, alcohols in 20% C_6D_6/CS_2. Data in parentheses are for alcohol complexes. [c] Proton attached to cationic center, methine proton for alcohols, ppm. [d] C1, ppm. [e] Broad multiplet, referenced to external H_3PO_4, ppm; where two signals are reported, major is first, minor is second. [f] Signals for the two diastereotopic methyl groups. Ph = C_6H_5, Me = CH_3, Pr^i = $CH(CH_3)_2$, and Bu^t = $C(CH_3)_3$.

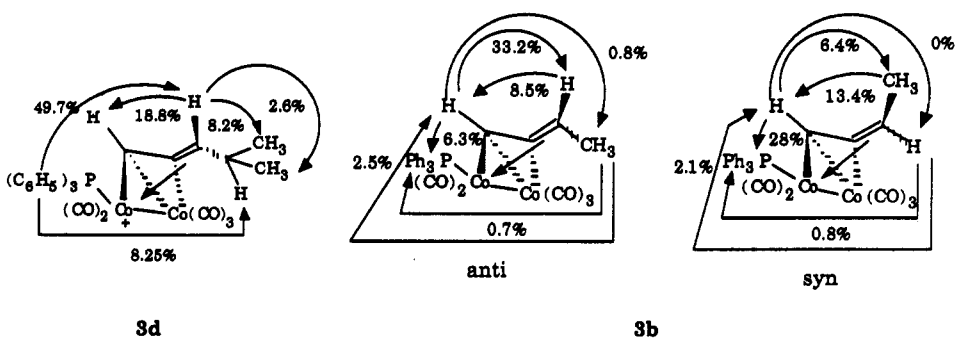


Figure 2. NOEDS enhancements for complexes **3d** and **3b**.

the parent $-Co_2(CO)_6$ cationic complexes 1[6g,8] is instructive. The metal–carbonyl IR stretching bands for the phosphinated cationic complexes **3** are found at higher frequency by approximately 15–30 cm^{-1} ($\Delta\nu$) compared to the alcohol complexes **2**. A similar shift, but of a larger magnitude ($\Delta\nu$ ca. 50 cm^{-1}), is found in proceeding from the $Co_2(CO)_6$-complexed alcohols to the corresponding cations **1**. The ^{1}H NMR spectra of **3** exhibit several interesting features. First, a number of the complexes (i.e. the secondary derivatives **3b,c,f,g**) exist as mixtures of two isomers (which slowly equilibrate; vide infra) as indicated by the presence of pairs of resonances for each proton; single isomers are observed in the spectra of the primary cation **3a**, secondary cations **3d,e,g**, and the tertiary ion **3i**. The chemical shift difference, $\Delta\delta$, for C1-H between the phosphinated cations and their alcohol precursors varies over a considerable range: for cations **3a–c,g,i** $\Delta\delta$ is remarkably small, ca. +0.1 to +0.2 ppm, whereas for the other complexes a larger downfield shift occurs, 1–3 ppm. The $\Delta\delta$ values for the parent $-Co_2(CO)_6$ system are typically about +1.5 ppm. The corresponding $\Delta\delta$ values in the ^{13}C NMR spectra for **3** also are variable, typically ca. +10 to +20 ppm, with no obvious correlation with structure but are smaller in magnitude than those observed for the $-Co_2(CO)_6$ derivatives **1** (ca. 15–75 ppm). Surprisingly, little or no change is seen in the ^{31}P NMR chemical shift between the alcohol (**2**) and the cationic (**3**) complexes.

Difference NOE experiments were carried out on the single isomeric isopropyl-substituted complex **3d** and the isomeric mixture of methyl-substituted complexes **3b** in order to further elucidate their solution structures (Figure 2). For the former, very large (19–50%) enhancements were observed between the resonances of the phosphine aromatic protons, the "acetylenic" C3-H, and the "propargylic" C1-H protons, whereas smaller enhancements (2–10%) were found between the resonances of the first two sets and those of the isopropyl group. These results indicate a closer proximity of C1-H to C3-H and the phosphine unit with the isopropyl group being more distant. The major isomer present initially in solutions of the butynyl complex **3b** was found to have the same stereochemistry as **3d** since a large enhancement was observed between C3-H and C1-H (33% when irradiating the former) but a very small enhancement (1%) between the C3-H and CH_3 at C1. The minor isomer exhibited the opposite behavior (and thus has the opposite stereochemistry); i.e., the C3-H/CH_3 NOE was much larger (6%) than the C3-H/C1-H interaction (0%).

Table II. Anti/Syn Isomerization of $[(R^1C_2CHR^2)Co_2(CO)_5PPh_3]BF_4$ (3)

compd	R^1	R^2	init ratio	K_{eq}	$\Delta G^{\ddagger}$	temp, K
3b	H	CH_3	8:1	1.320	19.4 (±2.0)	295
3c	H	C_6H_5	6:1	1.104	18.4 (±2.0)	295
3f	CH_3	CH_3	7:1	0.928	17.2 (±2.0)	253
3g	C_6H_5	CH_3	5:1	0.784	20.3 (±2.0)	295
3d	H	$CH(CH_3)_2$	>20:1	na		
3e	H	$C(CH_3)_3$	>20:1	na		
3h	C_6H_5	$CH(CH_3)_2$	>20:1	na		

For those alcohol complexes for which diastereomers have been isolated (**2b,c,f,g**) *either diastereomer produces the same isomeric mixture of cations 3 with considerable selectivity* (determined by ^{1}H NMR; Table II); i.e., *the cations are formed diastereoselectively but not diastereospecifically*. For those secondary precursors found only as single isomers (**2d,e,h**) only one cation isomer (**3d,e,h**) was found upon protonation. Long-term (3–6 h), low-

Table III. Stereoselectivity of Nucleophilic Quenching Reactions of 3

compd	R^1	R^2	T_1, °C[a]	T_2, °C[b]	Nu[c]	init[d]	final[e]	% de[f]
3c	H	C_6H_5	20	20	H_2O	(1*R**,2*S**,3*R**)	(1*S**,2*S**,3*R**)	66
			-78	20	H_2O	(1*S**,2*S**,3*R**)	(1*S**,2*S**,3*R**)	65
			-78	-78	OH^-[g]	(1*S**,2*S**,3*R**)	(1*S**,2*S**,3*R**)	61
			20	20	CH_3O^-[h]	(1*R**,2*S**,3*R**)	(1*S**,2*S**,3*R*)	51
3b	H	CH_3	-78	-78	CH_3OH	(1*R**,2*S**,3*R**)	(1*S**,2*S**,3*R*)	68
			-78	-78	CH_3OH	(1*S**,2*S**,3*R**)	(1*S**,2*S**,3*R*)	74
			-78	-78	CH_3O^-	(1*R**,2*S**,3*R**)	(1*S**,2*S**,3*R*)	57
			-40	-40	CH_3O^-	(1*R**,2*S**,3*R**)	(1*S**,2*S**,3*R*)	1[i]
3g	C_6H_5	CH_3	-78	-78	CH_3OH	(1*R**,2*S**,3*R**)	(1*S**,2*S**,3*R*)	75
3d	H	$CH(CH_3)_2$	-78	20	CH_3O^-	(1*R**,2*S**,3*R**)	(1*R**,2*S**,3*R**)	>99
3e	H	$C(CH_3)_3$	20	-78	CH_3OH	(1*R**,2*S**,3*R**)	(1*R**,2*S**,3*R*)	>99
			20	20	CH_3OH	(1*R**,2*S**,3*R**)	(1*R**,2*S**,3*R*)	>99
3h	C_6H_5	$CH(CH_2)_2$	20	20	CH_3OH	(1*R**,2*S**,3*R**)	(1*R**,2*S**,3*R**)	>99

[a] Cation formation temperature. [b] Quench reaction temperature. [c] Nu = nucleophile. [d] Configuration of initial alcohol. [e] Configuration of major product. [f] % de = % major - % minor. [g] Acetone/pH 9 buffer. [h] Methanol with excess sodium carbonate or stoichiometric sodium methoxide. [i] Quenched after 4 h at -40 °C.

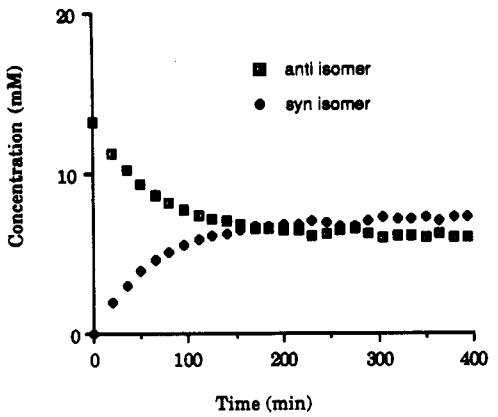


Figure 3. Isomerization of **3b** in acetone-d_6 at 263 K.

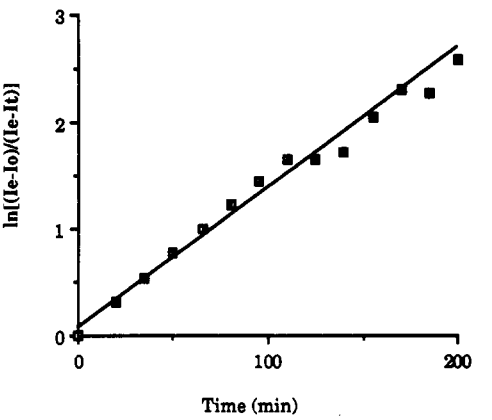


Figure 4. First-order plot for the isomerization of **3b** at 263 K. I_e is the peak integration at equilibrium, I_t is the peak integration at time t, and I_0 is the peak integration at time zero.

temperature NMR monitoring of the isomeric mixtures of complexes **3b,c,f,g** (in acetone-d_6) revealed a gradual change in the ratio of the isomers, approaching values of nearly one at equilibrium. The appearance/disappearance of pairs of resonances afforded concentration/time data (e.g. Figure 3) which exhibited good first-order behavior as illustrated in Figure 4 for the equilibration of complex **3b**. A plot of ln (I_e-I_o/I_e-I_t) vs time allows determination of k_1, k_{-1} (slope of line = $k_1 + k_2$; $K = k_1/k_2$), and $\Delta G^{\ddagger}$ via the Eyring equation (Table II). As can be seen from the data, the isomerization is a relatively high-energy process with similar $\Delta G^{\ddagger}$ values of 17–20 kcal/mol for the complexes examined.

The simple propargyl and the isopropyl-, *tert*-butyl-, and dimethyl-substituted complexes (**3a,d,e,h,i**) present as single isomers, showed no tendency to isomerize even after extended periods in solution. Moreover, ^1H NMR magnetization (spin saturation) transfer experiments on the primary and tertiary complexes **3a** and **3i**, involving irradiation of the inequivalent C1-H's or methyls, detected no magnetization transfer, indicating that dynamic processes which could exchange these groups are slow on the NMR time scale.

As noted earlier, Schreiber and co-workers provided NMR evidence for the existence of a second lower energy isomerization process for the $-Co_2(CO)_6$ complexes resulting in enantiomerization of chiral secondary cations.[6g] In an effort to detect the intervention of an enantiomerization/racemization process for the phosphinated derivatives, we conducted ^1H NMR spin saturation transfer experiments on the isopropyl complex **3d**. In the ^1H NMR spectrum of **3d** clearly separated resonances are observed for the diastereotopic methyl groups even at room temperature. If exchange between the diastereotopic groups is occurring on the NMR time scale, irradiation of the resonance for one group should cause transfer of magnetization to the other resulting in a signal decrease of the second. Using the inversion exchange technique with delays ranging from 0.001 to 2.00 s, we were unable to detect significant magnetization transfer in either acetone-d_6 or CD_2Cl_2 between -60 and +25 °C. Similarly, no noticeable line broadening of the methyl resonances was observed (hence, no enantiomerization on NMR time scale) up to 60 °C. These observations place a lower limit of ca. 21 kcal/mol[13] for processes which would cause exchange.

Cation Quenching with Nucleophiles. While formation of the phosphine-substituted cation salts **3** is a very facile process, their reactivity proved to be remarkably attenuated relative to their $-Co_2(CO)_6$ counterparts. Unlike the parent hexacarbonyl cations **1** which are hydrolyzed immediately in wet solvents, the phosphinated derivatives **3** react only slowly (3.5 h) with saturated aqueous sodium bicarbonate/THF at room temperature. Likewise, whereas the parent $-Co_2(CO)_6$ complexed cations react rapidly with ketones,[6k] acetone-d_6 proved to be a suitable NMR solvent for the phosphinated derivatives **3**. Reactions of **3** with either lithium or sodium methoxide are very fast, however, at any temperature.

Interestingly, *hydrolytic or methanolic quenching of the secondary cations* **3** *gave primarily* (for **3b,c,f,g**) *or exclusively* (for **3d,e,h**) *one isomer of the alcohol or methyl*

(13) Bovey, F. A. In *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Academic Press: San Diego, A, 1988; Chapter 5, p 297. Kegley, S. E.; Pinhas, A. R. In *Problems and Solutions in Organometallic Chemistry*; University Science Books: Mill Valley, CA, 1986; pp 20–26.

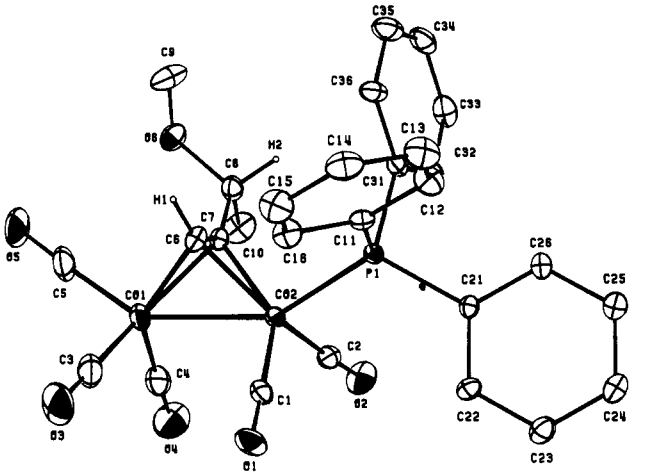
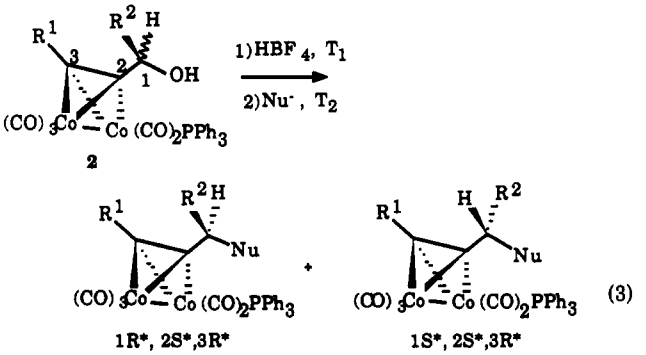


Figure 5. ORTEP diagram of the major isomer of **4b** obtained from methanol quenching of **3b**.

ether complex, regardless of the initial configuration of the alcohol used or the temperature for cation generation and quenching (eq 3; Table III). This stereoselectivity



qualitatively reflects the composition of the intermediate cations, i.e. isomeric cation mixtures give mixtures of quenched products and single cation isomers give only one quench isomer. The relative stereochemistry of the *major* isomers produced from hydroxide quenching of cations **3b,c,f,g** was found to be (1*S**,2*S**,3*R**) (numbering C1 as the hydroxyl-bearing carbon), i.e. the same as the less stable *minor* isomer produced in the original phosphination of the alcohol complexes. In contrast, aqueous quenching of the single isomeric cations **3d,e,h** regenerated the original (and only detected) (1*R**,2*S**,3*R**) alcohol isomer. The methoxide quenching results were found to be qualitatively the same, namely that a similar mixture of isomeric methyl ethers **4** was produced starting from either isomeric alcohol (for **3b,c,f,g**) and that the predominant product isomer was of the (1*S**,2*S**,3*R**) stereochemistry. This was confirmed by X-ray diffraction analysis in the case of the major isomer of **4b** obtained by methanol quenching of cation **3b** (Figure 5). Use of methanol, CH_3OH/Na_2CO_3, or $NaOCH_3$ did not appreciably affect the ratio of methyl ether products. However, allowing the cationic complex **3b** to stir for several hours in acetone at −40 °C prior to methoxide quenching gave an isomeric ratio (1:1) of **4b** very similar to that achieved in the NMR equilibrium experiments on **3b**, although the yield was reduced significantly.

To further elucidate the contrasting quenching behavior of the bulkier substituted derivatives **3d,e,h**, the structure of alcohol precursor **2e** was determined by X-ray diffraction. It can be seen from Figure 6 that the relative stereochemistry (and conformation) of **2e** (1*R**,2*S**,3*R**) is in fact *the same* as found for the major isomer of **2c**, consistent with our prior NMR and chromatographic correlations.[7]

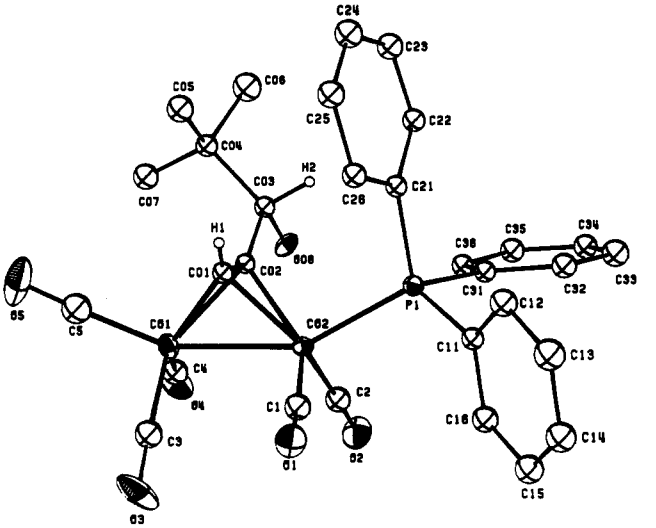


Figure 6. ORTEP diagram of the exclusive isomer of **2e**.

A survey of reactions of the phosphinated salt **3b** with several different carbon nucleophiles proved disappointing. Cyanide sources [KCN or $(CH_3CH_2)_2AlCN$] gave a mixture of products, none of which showed a nitrile band in the IR spectrum. Methylation was attempted, using methyl lithium, trimethyl aluminum, and dilithium cyano-2-thiophenylmethylcuprate, but produced either gross decomposition or only alcohol complexes after hydrolytic workup. Allyltrimethylsilane, 2-acetoxypropene, 2-acetoxystyrene, and 1-(trimethylsiloxy)cyclohexene, all of which readily couple with **1**, were unreactive toward **3b**. More potent carbon nucleophiles including lithium and sodium enolates of acetylacetone, cyclohexanone, acetophenone, and dimethyl malonate gave product mixtures, none of which was the alkylated product sought.

Discussion

The phosphine-substituted cation complexes **3** have been obtained in high yield by direct protonation of the precursor alcohol complexes, which, in turn, are efficiently prepared from the corresponding $-Co_2(CO)_6$ derivatives. Although we have not quantitatively assessed the thermodynamic stability of these cations (e.g. by pK_{R^+} measurements), their hydrolytic stability and low reactivity toward other weak nucleophiles (e.g. methanol, allyltrimethylsilane, acetone) compared to the parent $-Co_2(CO)_6$ complexes are indicative of an enhanced stability (lower reactivity) resulting from replacement of a weakly donating/strongly π-accepting CO ligand by the stronger donating/weaker accepting PPh_3. Further evidence for a more electron-rich complex cation in **3** comes from their IR spectra, which exhibit a smaller shift to higher frequency of the M–CO bands ($\Delta\nu$ ca. 30 cm^{-1}) relative to their precursor neutral complexes than observed for the parent complexes ($\Delta\nu$ ca. 50 cm^{-1}). Analogous changes in the ^1H and ^{13}C NMR spectra in proceeding from the alcohols to the cations ($\Delta\delta$'s) are also observed; i.e., the chemical shifts for the cationic species are generally at lower field than for the corresponding alcohols, but the quantitative effects are not uniform. This deshielding effect is expected on the basis of simple electron density concepts, but other factors including paramagnetic and anisotropy effects are often important contributors to the observed chemical shift. Very little difference was seen in the ^{31}P NMR spectra of the neutral and cationic complexes, apparently the result of mutually canceling

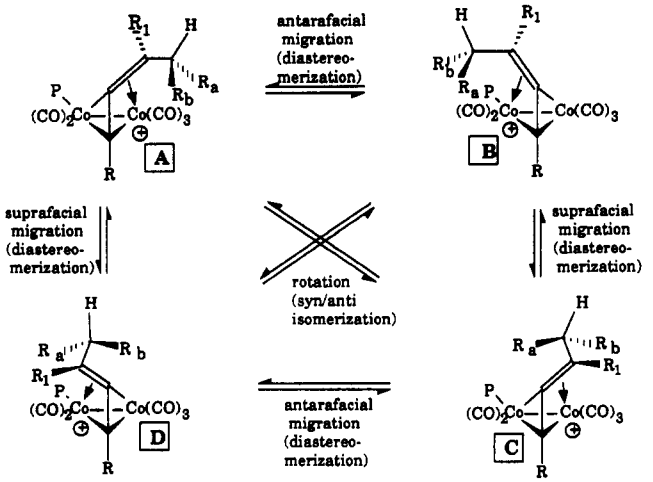


Figure 7. Isomerization pathways for $[(\mu\text{-}\eta^2,\eta^3\text{-}R^1C_2CR^2R^3)\text{-}Co_2(CO)_5PPh_3]^+$ (**3**).

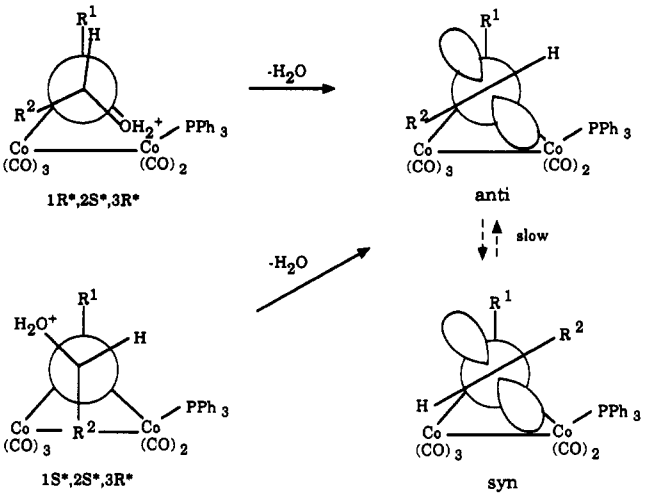


Figure 8. Stereoselective ionization of $[(\mu\text{-}\eta^2,\eta^2\text{-}R^1C_2C(OH)R^2R^3)Co_2(CO)_5PPh_3$ (**2**).

shielding/deshielding effects.

In considering the structures of these new cationic complexes, we use as our starting point the dynamic structural model proposed for the parent $-Co_2(CO)_6$ complexes (Figures 1[6g,8b] and 7). In the absence of X-ray diffraction results on the compounds **3**, our structural assignments are based on NMR studies and the assumption that the η^2,η^3-coordination mode for the bent propargyl ligand found for the isolobal Mo_2 derivatives[10] obtains for the phosphinated $-Co_2$ complexes. Inclusion of the phosphine ligand into the C_2Co_2 core unit introduces a new stereocenter so that *four diastereomeric structures* (A–D) *are possible* (vs two for the $-Co_2(CO)_6$ complexes) for secondary cations, i.e. R^2 = H and CHR_2 = alkyl or aryl. These include a pair (syn and anti, A and C) wherein the propargylic carbon (C1) interacts with the $-Co(CO)_3$ moiety and a second syn/anti pair (B and D) in which the $-Co(CO)_2(PPh_3)$ moiety serves this role. In fact, the complexes with smaller R^2 substituents (**3b,c,f,g**) have been found by NMR to exist in *only two* isomeric forms and those with bulky substituents (**3d,e,h**) exist over a wide temperature range as a *single* isomer. We propose that in these cases the cations have structures with the stronger donor $-Co(CO)_2(PPh_3)$ unit in the η^3-mode (B, D), primarily on the basis of the greatly attenuated reactivity of the complexes toward nucleophiles compared to the $-Co_2(CO)_6$ relatives. Examination of simple molecular models and the NOEDS results for complexes **3b** and **3d** are supportive of this assignment but alone are not definitive. The NOEDS experiments (Figure 2) clearly indicate an anti geometry [C3-H vs the R at C1] for both the ^{i}Pr-substituted complex (**3d**) and the initially predominant isomer of the Me-substituted complex **3b** since strong C3-H/C1-H enhancements are observed. The large C3-H/Me enhancements for the initially minor isomer of **3b** are then consistent with a syn geometry for this species.

The diastereo*selectivity* (but not *specificity*) observed in the formation of the cations is noteworthy; i.e., either isomeric alcohol (where available) produces the same isomeric mixture of cations. The fact that anti/syn isomerization is slow (vide infra) relative to cation formation indicates that the selectivity is kinetic in origin, arising in the ionization step. Given the relative stereochemistry established by X-ray diffraction for the major alcohol isomer of **2c**[7] and for the only isomer of **2e**, selective initial formation of the anti cation isomer is most easily accounted for by preferred ionization of the major (1*R**,2*S*,3*R**) alcohol from a syn-periplanar transition state, whereas the minor (1*S**,2*S**,3*R**) alcohol ionizes in an anti-periplanar mode (Figure 8). These arrangements minimize steric interactions between the C1-substituent and the bulky PPh_3 ligand and still allow some degree of a chimeric assistance by the $-Co(CO)_2(PPh_3)$ unit.

Several features must be accommodated in the mechanistic picture of the anti → syn cation isomerization process: (1) the reaction is first order in complex; (2) there is a relatively large energy barrier to isomerization (17–20 kcal/mol); (3) the ^{i}Pr- and ^{t}Bu-substituted cations exist as single isomers; (4) a significant solvent effect is observed (i.e. in all cases where isomerization occurs in acetone, there was no isomerization in CD_2Cl_2). Feature 1 is indicative of an intramolecular isomerization mechanism typical of a fluxional molecule. It is likely that isomerization occurs *without phosphine dissociation* since this process is very slow below room temperature for the neutral precursor complexes[7] and the electrophilic cationic complexes should be even less prone to dissociate the donor phosphine ligand.

The anti → syn isomerization requires a net 180° rotation of the $-CHR^+$ unit relative to the (alkyne)$Co_2(CO)_5PPh_3$ core (Figure 7). With the preferred geometry of the cations having the acceptor p-orbital of the $-CHR^+$ unit interacting preferentially with the more electron-rich $-Co(CO)_2(PPh_3)$ unit, syn/anti isomerization could be accomplished either via sequential "antarafacial"/"suprafacial" migration (C → D → B) or by direct 180° rotation (C → B). These two options are not unambiguously distinguished with the available data. The origin of the interesting and potentially useful solvent effect on isomerization may derive from involvement of the better donor solvent (i.e. acetone) in adduct formation at C1 or at a cobalt atom or by stabilization of an increasingly localized charge in the transition state.

It is instructive to compare the isomerization process and barriers for the phosphine-substituted derivatives **3** with those for the corresponding $-Co_2(CO)_6^+$ complexes **1**. In the latter system, the ease of isomerization increases with increasing substitution at the propargylic carbon, i.e. primary < secondary < tertiary. Thus, the parent propargyl complex, $(HC_2CH_2)Co_2(CO)_6^+$, has a static, unsymmetrical structure on the NMR time scale at 20 °C while the dimethyl-substituted complex, $(RC_2CMe_2)Co_2(CO)_6^+$, is "frozen out" only at reduced temperature ($\Delta G^\ddagger$ = 11 kcal/mol). The secondary cations, which show intermediate behavior, undergo enantiomerization (Figure 1) with a barrier of ca. 10 kcal/mol and anti/syn diastereomerization with a higher barrier, $\Delta G^\ddagger$ = 13 kcal/mol.

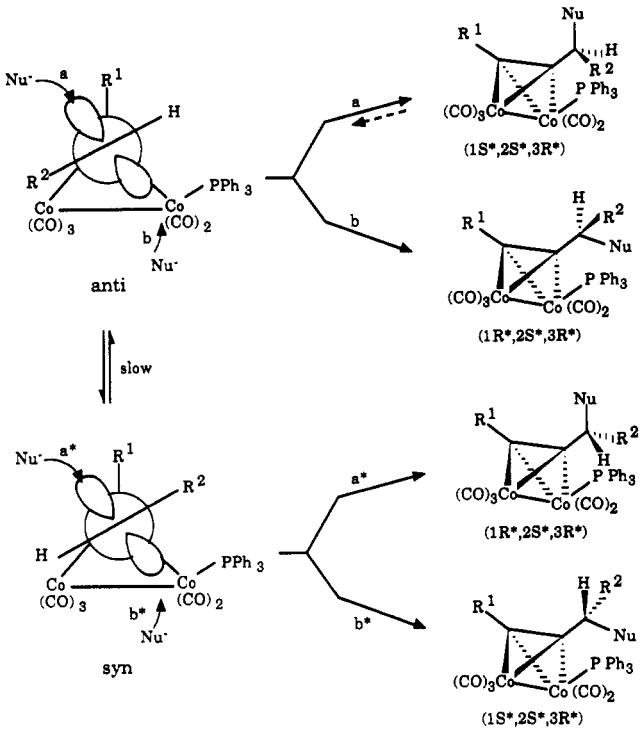


Figure 9. Stereochemical aspects of cation quenching.

Replacement of a CO ligand with PPh_3 as in **3** is found to increase isomerization energies in all measurable cases. Thus, the phosphinated primary and tertiary complexes, **3a** and **3i**, show no evidence of dynamic behavior or magnetization transfer, hence, must have a lower limit for anti → syn isomerization of at least 17 kcal/mol (vs 11 kcal for the 3° $-Co_2(CO)_6$ complex). Anti/syn isomerization for the phosphinated 2° cations **3b,f,g** occurs only slowly on the NMR time scale with an activation energy of ca. 18 kcal/mol (vs 13 kcal/mol for the $-Co_2(CO)_6$ derivatives). Enantiomerization (racemization) in the secondary systems of **3** (as probed by VT and SST experiments) was undetectable, giving a lower limit for this process of 21 kcal/mol. We note that such a process requires a combination of cluster core epimerization and antarafacial migration.[14] Since the former pathway likely has a relatively high barrier on the basis of our studies of the alcohol precursors to **3** (≥20 kcal/mol), we cannot determine the energetic contribution of the antarafacial migration component for comparison with the $-Co_2(CO)_6$ system.

The results of the quenching experiments support the above picture for the cationic complexes and provide further insight into the factors controlling the stereochemistry of nucleophilic addition. A number of observations indicate that the stereoselectivity observed in the quenching reactions of the less hindered cations **3b,c,f,g** is kinetic in origin; i.e., the quench isomer ratios reflect the preferred mode of attack on the isomer mixture present: (1) cation isomerization is slow relative to nucleophilic quenching; (2) both isomers react at similar rates (by low-temperature NMR monitoring); (3) the products are configurationally stable under the reaction conditions. For those complexes where R^2 is relatively small (CH_3, C_6H_5), the anti configuration of the cation is predominant initially and the stereochemistry of the major addition product is found to be (1*S**,2*S**,3*R**). This suggests a preferred approach of the nucleophile via pathway a (Figure 9), which probably is the least hindered side, away from the extremely bulky PPh_3 ligand. Similarly, preferred approach of nucleophile to the minor syn isomer via the more accessible a* direction produces largely the minor product isomer (1*R**,2*R**,3*S**). After equilibration, the cation complexes are in a ~1:1 ratio and nucleophilic addition then gives ca. a 1:1 mixture of quench products, with relatively more of the (1*R**,2*R**,3*S**) isomer arising via the syn cation and the a* channel.

To account for the specific formation of the original (1*R**,2*S**,3*R**) alcohol isomer when quenching the singly (anti) isomeric **3d,e,h**, we propose that the addition of nucleophile from the top side (a) is no longer the least hindered due to the steric bulk of the *tert*-butyl or isopropyl group. Attack from this direction may be either blocked or may be reversible (Figure 9), leading to ultimate product formation, the (1*R**,2*S**,3*S**) isomer, via pathway b. Consistent with this hypothesis we note (vide supra) that these particular cation complexes do not exist in the syn configuration and that the (1*S**,2*S**,3*R**) isomers of the alcohols **2d,e,h** have not been observed. A scale model of **2e** indicates that the steric interaction between the *tert*-butyl group and the phosphine phenyl rings is such that no conformation is energetically accessible for the complex with the (1*S**,2*S**,3*R**) stereochemistry.

The failure of the tested carbon nucleophiles to add cleanly to **3** is disappointing. The attenuated reactivity of **3** is reflected in their nonreactivity toward mild nucleophiles such as anisole, silylenol ethers, and allylsilanes. With more reactive nucleophiles such as enolates we presume that nonselective electron transfer, attack at the metal, or attack at the carbonyl ligands occurs.

Conclusions

Protonation of the chiral propargyl alcohol complexes **2** occurs readily and with moderate to high diastereoselectivity producing the corresponding cationic derivatives **3**. NMR analysis of **3** indicates that single, nonequilibrating isomers are produced from primary, tertiary, and those secondary alcohols bearing bulky substituents at C1 whereas syn/anti mixtures are obtained from less hindered secondary precursors (**2b,c,f,g**). The initially anti-enriched mixtures slowly convert to nearly equal anti/syn mixtures with a $\Delta G^{\ddagger}$ of 19.5 kcal/mol at 295 K for **3b**. The markedly increased isomerization barriers for the phosphinated derivatives **3** relative to their $-Co_2(CO)_6$ counterparts **1** offers future promise for achieving enantio- and diastereocontrol in their coupling reactions with nucleophiles. The cationic complexes **3**, however, have been found to be far less reactive toward nucleophiles than **1**. Quenching with oxygen nucleophiles including hydroxide and methoxide occurs in a moderately to completely stereoselective manner. For those cations which exist as isomeric mixtures, quenching before equilibration produces addition products enriched in the thermodynamically less stable (1*S**,2*S**,3*R**) isomer; quenching after equilibration affords an approximately 1:1 mixture of diastereomeric products. The single isomer cations **3d,e,h** are quenched to regenerate exclusively the original precursor alcohol complex. To date reactions with carbon nucleophiles have been unsuccessful. Efforts are now underway to produce a new generation of configurationally stable, but more reactive, chiral cationic complexes by incorporating bulky, weakly donating phosphite ligands.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of dry nitrogen. Solvents were dried and distilled in accordance with standard techniques. Diethyl ether was dried and distilled from sodium/benzophenone ketyl. $HBF_4 \cdot Et_2O$,

(14) We appreciate the insight of a reviewer who pointed this out.

acetone-d_6, and CD_2Cl_2 were used as purchased. Anhydrous HPF_6 was generated by the action of acetic anhydride on 60% aqueous acid. The (propargyl alcohol)$Co_2(CO)_5(PPh_3)$ complexes **2** were prepared as reported previously.[7] NMR spectra were recorded on a Varian XL 300 instrument, using standard programs for proton (299.9 MHz), carbon (75 MHz), and phosphorus (124 MHz) spectra. Kinetics data were collected using slight modifications of existing programs. The program INVEXC was used for the spin saturation transfer experiments;[15] data were statistically analyzed for significance.

Representative Preparation of $[(R^1C_2CR^2R^3)Co_2(CO)_5(PPh_3)]BF_4$ (3). $[(HC_2CH(C_6H_5))Co_2(CO)_5P(C_6H_5)_3]BF_4$ (3c). The following procedure is representative. Into a nitrogen-charged side-armed round-bottom flask equipped with stir bar, septum, and cannula was placed 0.100 g (0.153 mmol) of (3-phenyl-2-propyn-3-ol)pentacarbonyl(triphenylphosphine)dicobalt. After the septum was secured, the vessel was repeatedly degassed by the evacuate/backfill method. Anhydrous diethyl ether (5.00 mL) was added via syringe; the solution was cooled to −78 °C and degassed again. $HBF_4{\cdot}OEt_2$ (103 μL, 5.0 equiv) was added all at once via syringe followed by anhydrous diethyl ether (25 mL); the reaction mixture became murky and was allowed to stir for 2.5 h. At this time the complex salt was usually deposited on the walls of the flask as a dark red oil or solid. Filtration was accomplished via cannula, followed by repeated washing of the product with diethyl ether until the filtrate was colorless. Vacuum drying gave the product **3c** as a dark red solid (95%): mp 94 °C (dec); IR (THF) ν_{CO} 2065, 2005, 1995, 1965 (w) cm^{-1}; MS (FAB, Xe atoms generated at 3000 V, 1 mA; 3-nitrobenzyl alcohol) *m/e* 703 (M^+ − F, 4.46), 675 (M^+ − [F + CO], 6.44), 647 (M^+ − [F + 2CO], 74.57), 635 (M^+ − BF_4, 17.80), 607 (M^+ − [BF_4 + CO], 45.84), 579 (M^+ − [BF_4 + 2CO], 5.13), 551 (M^+ − [BF_4 + 3CO], 29.94), 523 (M^+ − [BF_4 + 4CO], 24.50), 495 (M^+ − [BF_4 + 5CO], 100), 321 ($CoP(C_6H_5)_3$, 64.34), 279 ([O]$P(C_6H_5)_3$ + 1, 8.51), 263 ($P(C_6H_5)_3$ + 1, 13.12), 262 ($P(C_6H_5)_3$, 5.6); ^1H NMR (acetone-d_6, 6:1 mixture of isomers) δ 8.41 and 8.10 ppm (s, sum 1 H, PHC*H*), 7.94–7.35 (m, 20 H, aromatic H), 7.25 (br s, overlap (?) singlets, 1 H, *HC*≡); ^{13}C NMR (acetone-d_6) δ 204.00, 203.88 (*CO*), 138.40–128.07 (aromatic C), 123.39 (*HC*≡), 106.10 (≡*CC*), 88.5 (*C*HPh); ^{31}P NMR (acetone-d_6, 1% H_3PO_4 external reference) δ 53.29 (br).

$[(HC_2CH_2)Co_2(CO)_5P(C_6H_5)_3]BF_4$ (3a). The complex was isolated in 97% yield: mp 129 °C (dec); IR (THF) ν_{CO} 2055, 2015 (sh), 2005, 1990, 1980 (sh) cm^{-1}; MS (FAB, Xe atoms generated at 3000 V, 1 mA; 3-nitrobenzyl alcohol) *m/e* 620 ([M + 2] − CO, 5.29), 592 ([M + 2] − 2CO, 10.32), 562 (M − 3CO, 6.15), 561 ([M + 2] − BF_4, 8.24), 532 ([M + 2] − 3CO, 7.63), 503 (M − [2CO + BF_4], 8.38), 475 (M − [3CO + BF_4], 24.64), 447 (M − [4CO + BF_4], 16.07), 419 (M − [5CO + BF_4], 100), 384 (M − $P(C_6H_5)_3$, 5.5), 321 ($CoP(C_6H_5)_3$, 96.64), 279 ([O]$P(C_6H_5)_3$, 22.89), 262 ($P(C_6H_5)_3$, 7.09); ^1H NMR (acetone-d_6) δ 8.31–7.55 (br m, 15 H, aromatic H), 5.43 (s, 1 H, *HC*≡), 3.39, 3.37 ppm (2 d, 1 H each, *J* = 14 Hz, CH_2); ^{13}C NMR (acetone-d_6) δ 219–218 (br, *CO*), 133.5–128.2 (aromatic C), 121.6 (*HC*≡), 88.2 ppm (CH_2), 79.7 (≡*CC*); ^{31}P NMR (acetone-d_6, 1% H_3PO_4 external reference) δ 57.17 (s).

$[(HC_2CHCH_3)Co_2(CO)_5P(C_6H_5)_3]BF_4$ (3b). The complex was isolated in 96% yield; mp 128 °C (dec); IR (THF) ν_{CO} 2075, 2005, 2000, 1995, 1865 (w) cm^{-1}; MS (FAB, Xe atoms generated at 3000 V, 1 mA; 3-nitrobenzyl alcohol) *m/e* 661 (M^+ + 1, 0.12), 641 (M^+ − F, 17.07), 632 (M^+ − CO, 6.98), 585 (M^+ + 1 − Ph, 80.43), 573 (M^+ −BF_4, 27.31), 545 (M^+ − [BF_4 + CO], 9.17), 517 (M^+ − [BF_4 + 2CO], 10.30), 489 (M^+ − [BF_4 + 3CO], 27.31), 461 (M^+ − [BF_4 + 4CO], 21.73), 433 (M^+ − [BF_4 + 5CO], 100), 398 (M^+ − $P(C_6H_5)_3$, 7.41); ^1H NMR (acetone-d_6, ~8:1 mixture of isomers) δ 7.74–7.44 (m) and 7.36 (bm 15 H, PPh_3), 5.58 and 5.32 (both d, 1 H, *HC*≡, J_{HP} = 5 Hz, major, and J_{HP} = 4 Hz, minor), 4.03 and 3.69 ppm (2 q, 1 H, *J* = 8 Hz for both CH_3), 1.19 and 1.04 ppm (2 d, 3 H, CH_3); ^{13}C NMR (acetone-d_6) δ 202, 195.3 (*CO*), 134.5–128.5 (aromatic C), 101.9 (*HC*≡), 97.3 (≡*CC*), 84.9 ($(CH_3)C^+$), 23.64 (CH_3); ^{31}P NMR (acetone-d_6, 1% H_3PO_4 external reference) δ 55.96 (minor) and 53.60 (major) (br s).

$[(HC_2CHCH(CH_3)_2)Co_2(CO)_5P(C_6H_5)_3]BF_4$ (3d). The complex was isolated in 97% yield: mp 103 °C (dec); IR (THF) ν_{CO} 2060, 2005, 1990, 1980 (sh) cm^{-1}; MS (FAB, Xe atoms generated at 3000 V, 1 mA; 3-nitrobenzyl alcohol) *m/e* 669 (M^+ − F, 11.75), 613 (M^+ − [F + 2CO], 39.83), 601 (M^+ − BF_4, 7.00), 583 (M^+ − [F + 2CO] − C_2H_6, 10.66), 573 (M^+ − [BF_4 + 2CO], 3.62), 517 (M^+ − [BF_4 + 3CO], 15.61), 508 (M^+ − [BF_3 + 4CO], 2.10), 506 (M^+ − [5CO + C_3H_6], 21.87), 489 (M^+ − [BF_4 + 4CO], 8.73), 488 (M^+ − [HBF_4 + 4CO], 20.54), 461 (M^+ − [BF_4 + 5CO], 42.73), 460 (M^+ − [HBF_4 + 5CO], 58.19), 436 ($Co(CO)_2P(C_6H_5)_3$, 10.50), 426 (M^+ − $P(C_6H_5)_3$, 3.60), 342 (M^+ − 3CO − $P(C_6H_5)_3$, 2.39); ^1H NMR (acetone-d_6) δ 7.99–7.35 (m, 15 H, aromatic H), 6.71 (d, 1 H, J_{HP} = 8.8 Hz, *HC*≡), 3.81 (d, 1 H, *J* = 8 Hz, ≡CC*H*), 1.53 ppm (m, 1 H, $CH(CH_3)_2$), 1.04 (d, 3 H, *J* = 8 Hz, CH_3) and 0.94 (d, 3 H, *J* = 8 Hz, CH_3); ^{13}C NMR (acetone-d_6) δ 206.0 (3 *CO*), 196.4 (2 *CO*), 134.1–130.4 (aromatic C), 119.4 (*HC*≡) 115.1 (≡*CC*$^+$), 88.8 (C^+HPr^i), 41.9 ($CH(CH_3)_2$), 26.1, 22.9 ($CH(CH_3)_2$); ^{31}P NMR (acetone-d_6, 1% H_3PO_4 external reference) δ 53.8 (br).

$[(HC_2CHC(CH_3)_3)Co_2(CO)_5P(C_6H_5)_3]BF_4$ (3e). The complex was isolated in 99% yield: mp 124 °C (dec); IR (THF) ν_{CO} 2060, 2010, 1990, 1980 (sh), 1945 (sh) cm^{-1}; MS (FAB, Xe atoms generated at 3000 V, 1 mA; 3-nitrobenzyl alcohol) *m/e* 634 (M^+ − BF_3, 16.5), 615 (M^+ − BF_4, 22.5), 583 (M^+ − [BF_4 + $2CH_4$], 25.8), 520 (M^+ − [$2C_6H_5$ + CO], 11.9), 492 (M^+ − [$2C_6H_5$ + 2CO], 16.9), 475 (M^+ − [BF_4 + 5CO], 16.2), 397 ([M^+ + 1] − [BF_4 + 5CO + H], 18.2), 373 (M^+ − [BF_3 + $P(C_6H_5)_3$], 27.4), 337 (M^+ − [BF_4 + (O)$P(C_6H_5)_3$], 46.2), 321 (co$P(C_6H_5)_3$, 58.4), 279 ([O]$P(C_6H_5)_3$, 100), 262 ($P(C_6H_5)_3$, 40.0); ^1H NMR (acetone-d_6) δ 7.85–7.52 (m, 15 H, PPh_3), 7.20 (overlapping s, 2 H, *HC*≡ and C*H*C$(CH_3)_3$), 1.05 (s, 9 H, C$(CH_3)_3$); ^{13}C NMR (acetone-d_6) δ 210, 196 (*CO*), 133.7–129.4 ppm (aromatic C), 106.5 (*HC*≡), 101.0 (≡C), 78.4 ($CCH(CH_3)_2$, 42.0 ($C(CH_3)_2$), 28.5 (C$(CH_3)_3$); ^{31}P NMR (acetone-d_6, 1% H_3PO_4 external reference) δ 53.60 (br).

$[(CH_3C_2CHCH_3)Co_2(CO)_5P(C_6H_5)_3]BF_4$ (3f). The complex was isolated in 96% yield: mp 52 °C (dec); IR (THF) ν_{CO} 2060, 2005, 1995, 1990 (sh), 1955; MS (FAB, Xe atoms generated at 3000 V, 1 mA; 3-nitrobenzyl alcohol) *m/e* 655 (M^+ − F, 16.91), 627 (M^+ − [F + CO], 14.6), 599 (M^+ − [F + 2CO], 100), 587 (M^+ − BF_4, 7.96), 559 (M^+ − [BF_4 + CO], 7.53), 531 (M^+ − [BF_4 + 2CO], 15.15), 503 (M^+ − [BF_4 + 3CO], 10.43), 475 (M^+ − [BF_4 + 4CO], 21.66), 447 (M^+ − [BF_4 + 5CO], 44.45), 412 (M^+ − $P(C_6H_5)_3$, 22.85), 397 (M^+ − [$P(C_6H_5)_3$ + CH_3], 31.37), 397 (M^+ − [$P(C_6H_5)_3$ + $2CH_3$], 23.56), 329 (M^+ − [$P(C_6H_5)_3$ + 3CO], 77.55), 312 ($CoP(C_6H_5)_3$, 86.61), 263 ($P(C_6H_5)_3$ + 1, 14.17), 262 ($P(C_6H_5)_3$, 7.74); ^1H NMR (acetone-d_6, isomeric mixture, 7:1) 7.68–7.4 (br m, 15 H, C_6H_5), 6.24 (q, 1 H, *J* = 6.4 Hz, C*H*CH_3, minor), 5.95 (q, 1 H, *J* = 6 Hz, C*H*CH_3, major), 2.18 (s, 3 H, CH_3C≡, major), 1.84 (s, 3 H, CH_3C≡, minor), 1.25 (d, 3 H, *J* = 6 Hz, CHCH_3, major), 1.19 (d, *J* = 6.4 Hz, CHCH_3, minor); ^{13}C NMR (acetone-d_6) δ 224 (3 *CO*), 215 (2 *CO*), 152.6 (*C*HCH$_3$), 146.7–122.6 (aromatic C), 98.0 (H_3CC≡), 74.6 (≡*CC*), 72.99 (CH_3C≡), other methyl beneath acetone; ^{31}P NMR (acetone-d_6, 1% H_3PO_4 external reference) δ 55.67 (major, br) and 57.26 (minor, br).

$[(C_6H_5C_2CHCH_3)Co_2(CO)_5P(C_6H_5)_3]BF_4$ (3g). The complex was isolated in 97% yield: mp 102°C (dec); IR (THF) ν_{CO} 2080, 2025 (sh), 2010, 1990, 1970 (sh) cm^{-1}; MS (FAB, Xe atoms generated at 3000 V, 1 mA; 3-nitrobenzyl alcohol) *m/e* 717 (M^+ − F, 5.32), 661 ([M^+ + 2] − C_6H_5, 93.97), 649 (M^+ − BF_4, 6.67), 621 (M^+ − [CO + BF_4], 7.87), 593 (M^+ − [2CO + BF_4], 13.07), 584 (M^+ − [3CO + BF_3], 5.88), 564 (M^+ − [3CO + BF_4], 15.16), 537 (M^+ −[4CO + BF_4], 39.67), 509 (M^+ − [5CO + BF_4], 52.37), 321 ($CoP(C_6H_5)_3$, 100), 279 ([O]$P(C_6H_5)_3$ + 1, 6.48), 263 ($P(C_6H_5)_3$ + 1, 19.64), 262 ($P(C_6H_5)_3$, 7.13); ^1H NMR (acetone-d_6; mixture of isomers, initial ratio ~5:1) δ 7.6–7.0 (m, 20 H, aromatic H), 4.18 and 4.05 (2 q, sum 1 H, *J* = 6 Hz, C*H*CH_3), 1.39 and 1.25 (2 d, sum 3 H, *J* = 6 Hz, CH_3); ^{13}C NMR (acetone-d_6) δ 208.50, 203.79 (*CO*), 191.305 (CH_3C^+), 139.9–135.5 (aromatic C), 124.3 (*HC*≡), 120.9 (≡*CC*), 110.4 (*C*H$(CH_3)_2$), 33.3, 28.7 ($CH(CH_3)_2$); ^{31}P NMR (acetone-d_6, 1% H_3PO_4 external reference) δ 53.2 (major, sh), and 52.1 (minor, sh).

$[(C_6H_5C_2CH(CH_3)_2)Co_2(CO)_5P(C_6H_5)_3]BF_4$ (3h). The complex was isolated in 96% yield: mp 66 °C (dec); IR (THF) ν_{CO} 2010, 2025 (sh), 2055 cm^{-1}; MS (FAB, Xe atoms generated at 3000 V, 1 mA; 3-nitrobenzyl alcohol) *m/e* 677 (M^+ − BF_4, 18.68), 649 (M^+ − [BF_4 + CO], 16.55), 621 (M^+ − [BF_4 + 2CO], 27.93), 593 (M^+ − [BF_4 + 3CO], 25.86), 565 (M^+ − [BF_4 + 4CO], 29.10), 537 (M^+ − [BF_4 + 5CO], 100), 321 ($CoP(C_6H_5)_3$, 50.48), 279 ($OP(C_6H_5)_3$ + 1, 5.64), 263 ($P(C_6H_5)_3$, 4.88); ^1H NMR (acetone-d_6) δ 7.6–7.2 (m, 20 H, C_6H_5), 6.02 (d, 1 H, *J* = 6, CH^+CH$(CH_3)_3$), 1.88 (m, 1

(15) Written by Prof. B.-M. Fung, University of Oklahoma.

H, $CH^+CH(CH_3)_3$), 1.36 (d, 3 H, $CH(CH_3)_3$, J = 7 Hz), 1.30 (d, 3 H, $CH(CH_3)_3$, J = 7 Hz); ^{13}C NMR (acetone-d_6); δ 208.4, 203.79 (CO), 191.3 (HC^+), 140.6–135.5 ppm (aromatic C), 124.3 ($C_6H_5C{\equiv}$), 120.9 ($\equiv CC$), 110.5 ($CH(CH_3)_2$), 33.3, 28.7 ($CH(CH_3)_2$); ^{31}P NMR (acetone-d_6, 1% H_3PO_4 external reference) δ 53.1 ppm (br).

[$(HC_2C(CH_3)_3)Co_2(CO)_6P(C_6H_5)_3$]$BF_4$ (3i). The complex was isolated in 96% yield: mp 122 °C (dec); IR (THF) ν_{CO} 2065, 2060, 2005, 1990, 1985 (sh) cm^{-1}; MS (FAB, Xe atoms generated at 3000 V, 1 mA; 3-nitrobenzyl alcohol) m/e 655 (M^+ – F, 13.60), 627 (M^+ – [F + CO], 15.6), 599 (M^+ – [F + 2CO], 64.8), 532 (M^+ – [BF_4 + 2CO], 8.6), 503 (M^+ – [BF_4 + 3CO], 8.4), 475 (M^+ – [BF_4 + 4CO], 13.8), 474 (M^+ – [HBF_4 + 4CO], 34.3), 447 (M^+ – [BF_4 + 5CO], 50.4), 446 (M^+ – [HBF_4 + 5CO], 100), 412 (M^+ – [BF_4 + $P(C_6H_5)_3$], 15.5), 321 ($CoP(C_6H_5)_3$, 69.27), 279 ([O]$P(C_6H_5)_3$ + 1, 8.5), 263 ($P(C_6H_5)_3$ + 1, 8.6); ^1H NMR (acetone-d_6) δ 7.63–7.37 (m, 15 H, PPh_3), 5.52 (d, 1 H, J_{HP} = 6 Hz, $HC{\equiv}$), 1.30 and 1.21 ppm (2 s, 3 H each, $C(CH_3)_2$); ^{13}C NMR (acetone-d_6) δ 205.3, 194.5 (CO), 134.9–129.3 (aromatic C), 113.3 ppm ($HC{\equiv}$), 84.1 ($C{\equiv}CC$), 80.1 ($(CH_3)_2C^+$), 34.2, 34.1 (CH_3); ^{31}P NMR (acetone-d_6, 1% H_3PO_4 external reference) δ 53.25 (br s).

Spin Saturation Transfer Experiments. Spin saturation transfer experiments were performed on a Varian XL 300-MHz instrument, using the INVEXC program, written by Dr. B.-M. Fung of the University of Oklahoma. This program is a variation on selective population inversion spectroscopy. Five variables are used: (1) a long (10 s or more) relaxation delay, followed by (2) a 180° pulse specific to one of the signals to be investigated, then (3) a delay that is varied (usually between 0.001 and 2.00 s), then (4) a 90° general pulse, then (5) a delay equal to $^1/_2\Delta n$, where n is the $\delta\Delta$ value of the two signals to be investigated, and finally (6) another 90° general pulse, followed by acquisition.

Water Quenching Reactions of 3. Into a nitrogen-charged side-arm round-bottom flask equipped with a stir bar and septum was placed 0.136 mmol of compound **3** and 10 mL of acetone. At this point one of the following procedures was used: (1) cool the reaction mixture to −41 °C; (2) cool the reaction mixture to −78 °C; (3) maintain the reaction mixture at room temperature. Then quenching was effected by addition of 25 mL of freshly prepared degassed 5:1 acetone: aqueous quench solution via cannula at whichever reaction temperature was being employed. The quench solutions were either aqueous saturated sodium carbonate pH 7 (phosphate/borate) or pH 9 buffers. The reaction was allowed to stir at the indicated temperature for 30 min and then examined via TLC (silica gel 60, 4:1 pentane/diethyl ether). Stirring and TLC monitoring were continued until no evidence of cation remained. The solvent was removed in vacuo, and the resulting residue was extracted thrice with 10-mL aliquots of diethyl ether. The combined ether portions were dried over magnesium sulfate, and the solvent was evaporated at reduced pressure. Trace amounts of ether were removed via the freeze/pump/thaw method. The products were subjected to NMR analysis without further purification. Product identity and isomer ratios were established by comparison with spectra of the authentic[7] complexes and integration of corresponding pairs of resonances.

Methanol Quenching Reactions of 3. The following procedure is general. Into a nitrogen-charged side-arm round-bottom flask equipped with stir bar and septum was placed 0.138 mmol of the complex **3** followed by repeated degassing (via the pump/backfill method). Into a second nitrogen-charged vessel was placed either 5 equiv of anhydrous Na_2CO_3 in 15 mL of anhydrous methanol (distilled from magnesium) or 1–5 equiv of sodium methoxide in methanol. The two flasks were then either cooled to −78 °C or −41 °C or maintained at ambient temperature. The methanol mixture was then transferred into the flask containing **3** via cannula, and the reaction was allowed to stir under nitrogen with TLC monitoring (20% diethyl ether in pentane; starting cation does not migrate and is visible at the origin after color development with iodine). When the reaction was deemed complete, the solvent was removed in vacuo, the resulting residue was extracted thrice with diethyl ether (15 mL each), the ether was evaporated in vacuo, and the product mixture analyzed by NMR (integrating the respective methoxy or methine resonances of the isomers) or separated by PTLC (silica gel 60, 1:99 diethyl ether/pentane).

(2*R,3*S**,4*R**)-[Pentacarbonyl(μ-η²,η²-2-methoxy-3-butyne)(triphenylphosphine)dicobalt(*Co–Co*)] (4b):** MS (FAB, Xe atoms generated at 3000 V, 1 mA; 3-nitrobenzyl alcohol) m/e 604 (M^+, 1.5), 573 (M^+ – OCH_3, 1.5), 548 (M^+ – 2CO, 14.3), 520 (M^+ – 3CO, 16.8), 492 (M^+ – 4CO, 43.4), 464 (M^+ – 5CO, 73.8), 433 (M^+ – [5CO + OCH_3], 8.4), 391 (M^+ – [CO + OCH_3 + $2C_6H_5$], 38.4), 321 (Co – $P(C_6H_5)_3$, 26.5), 279 ([O]$P(C_6H_5)_3$ + 1, 34.4), 263 ($P(C_6H_5)_3$ + 1, 3.2); ^1H NMR (20% C_6D_6 in CS_2) δ 7.4–7.1 (m, 15 H, C_6H_5), 5.19 (d, 1 H, J_{H-P} = 3 Hz, $HC{\equiv}$), 3.18 (1, 1 H, J_{H-H} = 6 Hz, $CH(OCH_3)CH_3$), 2.76 (s, 3 H, OCH_3), 1.35 (d, 3 H, J_{H-H} = 6 Hz, $CH(OCH_3)CH_3$); ^{13}C NMR (20% C_6D_6 in CS_2) δ 202 (CO), 201 (CO), 135–128 (C_6H_5), 105 ($HC{\equiv}$), 93.5 ($\equiv C$), 75.9 ($C(OCH_3)$, 56.0 (OCH_3), 30.46 (CH_3).

(2*S,3*S**,4*R**)-[Pentacarbonyl(μ-η²,η²-2-methoxy-3-butyne)(triphenylphosphine)dicobalt(*Co–Co*)] (4b′):** MS (FAB, Xe atoms generated at 3000 V, 1 mA; 3-nitrobenzyl alcohol) m/e 573 (M^+ – OCH_3, 2.6), 548 (M^+ – 2CO, 9.9), 520 (M^+ – 3CO, 14.5), 492 (M^+ – 4CO, 53.0), 464 (M^+ – 5CO, 100) 433 (M^+ – [5CO + OCH_3], 6.9), 321 ($CoP(C_6H_5)_3$, 33.6), 279 ([O]$P(C_6H_5)_3$ + 1, 26.5), 262 ($P(C_6H_5)_3$, 3.3); ^1H NMR (20% C_6D_6 in CS_2) δ 7.45–7.05 (m, 15 H, C_6H_5), 4.86 (d, 1 H, J_{H-P} = 2 Hz, $HC{\equiv}$), 3.49 (q, 1 H, J_{H-H} = 9 Hz, $CH(OCH_3)CH_3$), 3.09 (s, 3 H, OCH_3), 1.04 (d, 3 H, J_{H-H} = 9 Hz, $CH(OCH_3)CH_3$); ^{13}C NMR (20% C_6D_6 in CS_2) δ 203, 202 (CO), 133–127 (C_6H_5), 110 ($HC{\equiv}$), 93.2 ($\equiv C$), 72.9 ($C(OCH_3)$, 55.9 (OCH_3), 23.5 (CH_3).

(2*R,3*S**,4*R**)-[Pentacarbonyl(μ-η²,η²-4-phenyl-2-methoxy-3-butyne)(triphenylphosphine)dicobalt(*Co–Co*)] (4g):** IR (THF) 2060, 2005, 1995, 1965, 1090 cm^{-1}; MS (FAB, Xe atoms generated at 3000 V, 1 mA; 3-nitrobenzyl alcohol, mixture of isomers) m/e 680 (M^+, 0.8), 649 (M^+ – OCH_3, 1.2), 624 (M^+ – 2CO, 11.5), 621 (M^+ – [CO + OCH_3], 0.2) 596 (M^+ – 3CO, 3.2), 593 (M^+ – [2CO + OCH_3], 0.3), 568 (M^+ – 4CO, 31), 565 (M^+ – [3CO + OCH_3], 0.6), 540 (M^+ – 5CO, 55.3), 509 (M^+ – [5CO + OCH_3], 4.3), 321 ($CoP(C_6H_5)_3$, 17.4), 279 ($OP(C_6H_5)_3$ + 1, 100), 262 ($P(C_6H_5)_3$, 5.3); ^1H NMR (20% C_6D_6 in CS_2) δ 7.2–6.8 (m, 20 H, C_6H_5), 3.54 (q, 1 H, J_{H-H} = 6 Hz, $CH(OCH_3)$), 2.95 (s, 3 H, $CH(OCH_3)$), 1.38 (d, 3 H, J_{H-H} = 6 Hz, $CH(OCH_3)CH_3$); ^{13}C NMR (20% C_6D_6 in CD_2) δ 205, 201 (CO), 134.9–126.5 (C_6H_5), 96.5 ($C_6H_5C{\equiv}$), 75.4 ($\equiv CH(OCH_3)CH_3$), 66.0 (OCH_3), 55.2 ($C(OCH_3)CH_3$), 20.97 ($C(OCH_3)CH_3$).

(2*S,3*R**,4*S**)-[Pentacarbonyl(μ-η²,η²-4-phenyl-2-methoxy-3-butyne)(triphenylphosphine)dicobalt(*Co–Co*)] (4g′):** IR (THF) ν_{CO} 2060, 2005, 1990, 1965, 1090 cm^{-1}; MS (FAB, Xe atoms generated at 3000 V, 1 mA; 3-nitrobenzyl alcohol) m/e 680 (M^+, 0.8), 649 (M^+ – OCH_3, 1.2), 624 (M^+ – 2CO, 11.5), 596 (M^+ – 3CO, 3.2), 568 (M^+ – 4CO, 31), 540 (M^+ – 5CO, 55.3), 321 ($CoP(C_6H_5)_3$, 17.4), 279 ([O]$P(C_6H_5)_3$ + 1, 100), 262 ($P(C_6H_5)_3$, 5.3); ^1H NMR (20% C_6D_6 in CS_2) δ 7.35–6.85 (m, 20 H, C_6H_5), 4.85 (q, 1 H, J_{H-H} = 6 Hz, $CH(OCH_3)CH_3$), 3.12 (s, 3 H, $CH(OCH_3)CH_3$), 1.15 (d, 3 H, J_{H-H} = 6 Hz, $CH(OCH_3)CH_3$); ^{13}C NMR (20% C_6D_6 in CS_2) δ 205, 201 (CO), 134.9–126.5 (C_6H_5), 94.5 ($C_6H_5C{\equiv}$), 76.5 ($\equiv CH(OCH_3)CH_3$), 66.0 (OCH_3), 56.6 ($C(OCH_3)CH_3$), 21.3 ($C(OCH_3)CH_3$).

(1*R,2*S**,3*R**)-[Pentacarbonyl(μ-η²,η²-1-methoxy-1-phenyl-2-propyne)(triphenylphosphine)dicobalt(*Co–Co*)] (4c):** IR (thin film) ν_{CO} 2065, 2005, 2000, 1975 (sh), 1915, 1090 cm^{-1}; ^1H NMR (20% C_6D_6 in CS_2) δ 7.4–7.15 (m, 15 H, $P(C_6H_5)_3$), 6.95 (d, 3 H, J_{H-H} = 7 Hz, C_6H_5), 6.58 (d, 1 H, J_{H-H} = 2.4 Hz, C_6H_5), 6.55 (d, 1 H, J_{H-H} = 2.4 Hz, C_6H_5), 4.62 (d, 1 H, J_{H-P} = 3 Hz, $HC{\equiv}$), 4.20 (s, 1 H, $C(OCH_3)HC_6H_5$), 3.11 (s, 3 H, OCH_3).

(1*S,2*S**,3*R**)-[Pentacarbonyl(μ-η²,η²-1-methoxy-1-phenyl-2-propyne)(triphenylphosphine)dicobalt(*Co–Co*)] (4c′):** IR (thin film) ν_{CO} 2065, 2005, 2000, 1975 (sh), 1085 cm^{-1}; ^1H NMR (20% C_6D_6 in CS_2) δ 7.42–6.93 (m, 20 H, C_6H_5), 5.1 (d, 1 H, J_{H-P} = 4.6 Hz, $HC{\equiv}$), 4.35 (s, 1 H, $C(OCH_3)HC_6H_5$), 2.71 (OCH_3).

X-ray Diffraction of 2e and 4b. Single crystals of both **4b** and **2e** were obtained by recrystallization from diethyl ether. Saturated solutions were prepared at room temperature and cooled to −10 °C for ca. 20 min. After filtration of an initial crude material, the filtrate was recooled to −20 °C for a further 30 min, affording X-ray-quality crystals. X-ray crystal data for **4b**: Data collected at 22 °C; $C_{28}H_{23}Co_2O_6P$, fw = 604.3, space group $P\bar{1}$; a = 8.870 (2) Å, b = 12.116 (3) Å, c = 13.676 (3) Å, V = 1381.7 Å³, Z = 2, D_c = 1.453 g cm^3, $F(000)$ = 616, λ(Mo Kα) = 0.710 69 Å, μ(Mo Kα) = 12.9 cm^{-1}. Cell dimensions and intensities of 4361 reflections ($2\theta_{max}$ = 50°) were measured. The structure was solved by the heavy-atom method, and all non-hydrogen atoms were

refined anisotropically. All calculations were carried out using the SHELX-76 program. For 2928 unique observed reflections [$I > 2\sigma(I)$] the final $R = 0.036$, $R_w = 0.042$, and GOF = 1.4. Full details of the structure determination are available as supplementary material. X-ray crystal data for **2e**: Data collected at 22 °C; $C_{30}H_{27}Co_2O_6P$, fw = 632.38, space group $P2_1/n$, $a = 9.352$ (2) Å, $b = 20.174$ (4) Å, $c = 31.646$ (5) Å, $V = 5925.8$ Å^3, $Z = 8$, $D_c = 1.418$ g cm^3, $F(000) = 2592$, λ(Mo Kα) = 0.710 69 Å, μ(Mo Kα), = 12.1 cm^{-1}. Cell dimensions and intensities of 10 387 reflections ($2\theta_{max} = 50°$) were measured. The structure was solved by the heavy-atom method, and all non-hydrogen atoms were refined anisotropically. All calculations were carried out using the SHELX-76 program. For 3168 unique observed reflections [$I > 2\sigma(I)$] the final $R = 0.052$, $R_w = 0.048$, and GOR = 1.2. Only one of the two virtually identical independent molecules in the asymmetric unit is shown in the ORTEP diagram. Only the Co, P, and O atoms were refined anisotropically; all the C atoms were refined isotropically. Full details of the structure determination are available as supplementary material.

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Registry No. **2a**, 141610-08-4; **2b** (isomer 1), 118576-64-0; **2b** (isomer 2), 118628-34-5; **2c** (isomer 1), 118576-65-1; **2c** (isomer 2), 118628-35-6; **2d**, 141527-15-3; **2e**, 118576-66-2; **2f** (isomer 1), 141527-16-4; **2f** (isomer 2), 141610-20-0; **2g** (isomer 1), 118710-59-1; **2g** (isomer 2), 118576-68-4; **2h**, 118576-67-3; **2i**, 141527-17-5; **3a**, 141527-19-7; *anti*-**3b**, 141527-21-1; *syn*-**3b**, 141610-10-8; *anti*-**3c**, 141527-23-3; *syn*-**3c**, 141610-12-0; *anti*-**3d**, 141527-25-5; *anti*-**3e**, 141527-27-7; *anti*-**3f**, 141527-29-9; *syn*-**3f**, 141610-14-2; *anti*-**3g**, 141527-31-3; *syn*-**3g**, 141610-16-4; *anti*-**3h**, 141527-33-5; **3i**, 141527-35-7; **4b**, 141527-36-8; **4b'**, 141610-17-5; **4c**, 141527-37-9; **4c'**, 141610-18-6; **4d**, 141527-39-1; **4e**, 141527-40-4; **4g**, 141527-38-0; **4g'**, 141610-19-7; **4h**, 141527-41-5.

Supplementary Material Available: Tables of complete X-ray crystal data, refinement parameters, positional parameters, and bond lengths and angles for **4b** and **2e** (21 pages). Ordering information is given on any current masthead page.

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Lewis-Acid-Promoted Decarbonylation of Coordinated Carbon Dioxide: Reactions of $(\eta^5\text{-}MeC_5H_4)_2Nb(\eta^2\text{-}CO_2)CH_2SiMe_3$ with Lewis Acids

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The interaction of $Cp'_2Nb(\eta^2\text{-}CO_2)CH_2SiMe_3$ (**1**; Cp' = η^5-MeC_5H_4) with several Lewis acids has been studied and found to result in facile decarbonylation of **1**; the Nb-containing products depend markedly on the Lewis acid partner. Reaction of **1** with $LiPF_6$ or $BF_3{\cdot}Et_2O$ causes both decarbonylation and deoxygenation, producing $[Cp'_2Nb(F)CH_2SiMe_3]Z$ [Z = PF_6^- (**3**), BF_4^- (**6**)], which have been characterized spectroscopically and (for **3**) by X-ray diffraction; **3** is also produced in the reaction of the oxo derivative $Cp'_2Nb(O)CH_2SiMe_3$ (**2**) with $LiPF_6$ or $BF_3{\cdot}Et_2O$. **1** reacts with $ZnCl_2$ first to form an adduct, $Cp'_2Nb(CO)_2CH_2SiMe_3{\cdot}ZnCl_2$ (**7**), which based on IR and NMR data appears to have a novel μ-CO_2 unit bridging Nb and Zn. Complex **7** is unstable, decomposing with CO loss to form $[Cp'_2Nb(CH_2SiMe_3)O{\cdot}ZnCl_2]_2$ (**8**), an adduct of $ZnCl_2$ with the oxo species **2**, which has been characterized crystallographically; **8** is also produced from **2** and $ZnCl_2$. Reaction of **1** with $HgCl_2$ rapidly produces an incompletely characterized product **10**, which has been both decarbonylated and dealkylated. Although $CdCl_2$ does not react with **1** under comparable conditions, Me_3SiCl reacts rapidly with **1** to produce $Cp'_2Nb(O)Cl$ (**11**), resulting from decarbonylation and dealkylation; the structure of **11** has been established by X-ray diffraction.

Introduction

Expanding interest in transition metal-mediated chemical[1] and electrochemical[2] transformations of carbon dioxide has stimulated efforts to elucidate the reactivity of coordinated CO_2.[3] In this context, we reported recently the first example of photoinduced CO_2 disproportionation in the complex $Cp_2Mo(\eta^2\text{-}CO_2)$[4] and its dark reactions with electrophilic agents[5] and transition metal hydrides[6] which

(1) Reviews: (a) Inoue, S.; Yamazaki, Y. *Organic and Bio-organic Chemistry of Carbon Dioxide*; Kodansha Ltd.: Tokyo, 1982; Chapter 3. (b) Eisenberg, R.; Hendrickson, D. E. *Adv. Catal.* **1979**, *28*, 79. (c) Darensbourg, D.; Kudaroski, R. A. *Adv. Organometal. Chem.* **1983**, *22*, 129; (d) Walther, D. *Coord. Chem. Rev.* **1987**, *79*, 135. (e) Kolomnikov, I. S.; Lysyak, T. V. *Russ. Chem. Rev.* **1990**, *59*, 344. (f) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: Weinheim, FRG, 1988.

(2) Reviews: ref 1e. *Catalytic Activation of Carbon Dioxide*; ACS Symposium Series No. 363; Ayers, W. M., Ed.; American Chemical Society: Washington, DC, 1988; Chapters 5 and 6.

(3) (a) Harlow, R. L.; Kinney, J. B.; Herskovitz, T. *J. Chem. Soc., Chem. Commun.* **1980**, 813. (b) Forschner, T.; Menard, K.; Cutler, A. R. *J. Chem. Soc., Chem. Commun.* **1984**, 121. (c) Giuseppetti, M. E.; Cutler, A. R. *Organometallics* **1987**, *6*, 970. (d) Gibson, D. H.; Ong, T. S. *J. Am. Chem. Soc.* **1987**, *109*, 7191. (e) Senn, D. R.; Gladysz, J. A.; Emerson, K.; Larsen, R. D. *Inorg. Chem.* **1987**, *26*, 2737. (f) Maher, J. M.; Lee, G. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 6797. (g) Ito, T.; Yamamoto, A. *J. Chem. Soc., Dalton Trans.* **1975**, 1398.

(4) Belmore, K. A.; Vanderpool, R. A.; Tsai, J.-C.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1988**, *110*, 2004.

(5) Tsai, J.-C.; Khan, M.; Nicholas, K. M. *Organometallics* **1989**, *8*, 2967.

0276-7333/92/2311-2607$03.00/0