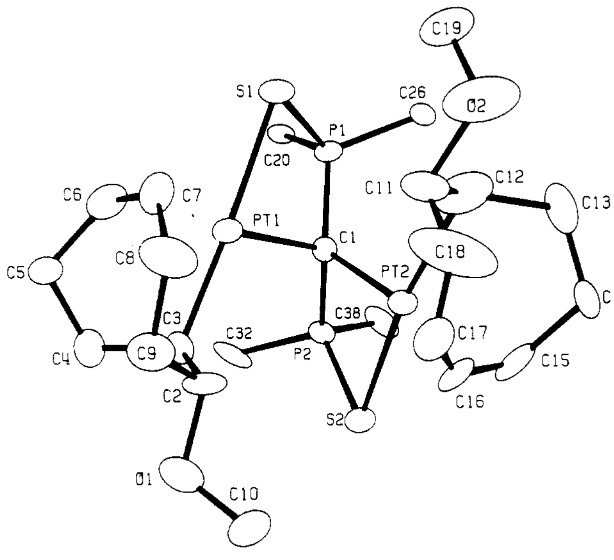

Figure 1. Molecular structure of VIII, $[Pt_2\{Ph_2P(S)CP(S)Ph_2\}(MeOcod)_2]$. For clarity, only one carbon is shown for each of the four phenyl rings.

toluene-d_8 solution ^{13}C and ^{31}P NMR evidence[19] indicates an S,S-bonded structure, but in more polar solvents, such as $CDCl_3$ or tetrahydrofuran-d_8, rapid exchange of the two phosphorus environments occurs at ambient temperatures and slow exchange limit ^{31}P spectra are not obtained until -70 °C. Line-shape analysis gives $\Delta G^{\circ\ddagger}$ as 49 kJ mol^{-1} in tetrahydrofuran. Interestingly, the corresponding methyl-substituted complex $[Pt\{Ph_2P(S)CMeP(S)Ph_2\}(MeOcod)]$[20] shows no dynamic exchange at ambient temperatures, and the ^{31}P spectrum in dimethyl-d_6 sulfoxide does not coalesce until 60 °C ($\Delta G^{\circ\ddagger} = 66$ kJ mol^{-1}). If exchange occurs by dissociation of one end of the bound ligand followed by reorganization of the three-coordinate platinum intermediate before recoordination of the ligand, then a determining factor in these rates could be solvation of the "dangling" P═S group in the intermediate. It is not clear, however, why the presence of a methyl group should have such a large influence on this process.

The subsequent reactivity of VII is a combination of ligand- and metal-centered processes with gradual formation of a novel dimer, VIII, in which $[C\{P(S)Ph_2\}_2]^{2-}$ forms a quaternary carbon bridge between two platinum centers.[21] The bridging carbon is part of four-member, C,S chelate rings at both platinums. An X-ray diffraction study (Figure 1)[22] shows the two approximately square-planar platinum centers inclined at 90.1° to each other and a very distorted tetrahedron around carbon with P–C–P = 127.2° and the other angles ca. 94°. The complex is remarkable both as the first example of a complexed $[C\{P(S)Ph_2\}_2]^{2-}$ ion and as a disubstituted methylene-bridged species. Methylene bridges which are unsupported by metal–metal bonds are relatively rare,[23] as are methylene bridges of any type between platinum atoms.[23,24] The concept of linking metal centers with a strongly bound bridge accompanied by relatively labile[10,25] pendant arms may lead to unusual chemistry both at the metals and at the bridge.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for a research grant.

Supplementary Material Available: Tables of fractional atomic coordinates, anisotropic temperature parameters, interatomic distances, bond angles, and selected intermolecular distances (8 pages); a listing of structure factors (10 pages). Ordering information is given on any current masthead page.

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(19) VII: $\delta(C_A)$ 15.6 ppm, $^1J(C_A–P) = 96$ Hz, $^2J(C_A–Pt) = 96$ Hz, $\delta(C_B)$ 33.2 ppm, $^1J(C_B–Pt) = 638$ Hz, $\delta(C_{C/D})$ 85.5/88.4 ppm, $^1J(C_{C/D}–Pt) = 184/181$ Hz; $\delta(P_A)$ 33.8 ppm, $^2J(Pt–P_A) =$ ca. 50 Hz, $\delta(P_B)$ 38.1 ppm, $^2J(Pt–P_B) = 125$ Hz, $J(P–P) = 11$ Hz.

(20) $\delta(C_A)$ 14.6 ppm, $^1J(C_A–P) = 108$ Hz, $^2J(C_A–Pt) = 64$ Hz, $\delta(C_B)$ 33.7 ppm, $^1J(C_B–Pt) = 625$ Hz, $\delta(C_{C/D})$ 84.6/87.9 ppm, $^1J(C_{C/D}–Pt) = 188/186$ Hz; $\delta(P_A)$ 33.5 ppm, $^2J(Pt–P_A) = 42$ Hz, $\delta(P_B)$ 38.6 ppm, $^2J(Pt–P_B) = 107$ Hz, $J(P–P) = 51$ Hz.

(21) VIII: $\delta(P)$ 48.33 ppm, $J(P–Pt) = 337$ and 12.2 Hz, $J(P–P) = 23.9$ Hz.

(22) Crystal data at 25 °C: monoclinic, space group C2/c (No. 15); $a = 19.033$ (4), $b = 14.145$ (4), $c = 29.794$ (4) Å; $\beta = 99.49$ (2)°; V(cell) = 7911.23 Å^3; $D_{measd} = 1.83$ g cm^{-3} (flotation in $CCl_4/CHBr_3$), $D_{calcd} = 1.87$ g cm^{-3}; formula $C_{43}H_{50}O_2P_2Pt_2S_2$; $M_r = 1115.12$; $Z = 8$. Asymmetric unit = one molecule. Intensity measurements were collected for two reciprocal space octants (h unrestricted, $k \geq 0$, $l \geq 0$) up to $2\theta = 50°$ on a CAD-4 diffractometer and corrected for Lorentz, polarization, and absorption effects. Refinement was by full-matrix least-squares calculations of 455 variable parameters based on 2188 independent reflections to give $R = 0.040$ and $R_w = 0.040$ at the present stage of refinement. Details are given in the supplementary material.

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(25) Browning, J.; Beveridge, K. A.; Bushnell, G. W.; Dixon, K. R. *Inorg. Chem.* **1986**, *25*, 1987–1992.

Diastereoselective Synthesis of Chiral Clusters from the Reaction of Chiral (Propargyl alcohol)$Co_2(CO)_6$ with Triphenylphosphine

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Received September 6, 1988

Summary: Dicobalt hexacarbonyl complexes of chiral (racemic) propargylic alcohols **1** react with PPh_3 to form the diastereomeric complexes $[R^1C{\equiv}CCH(OH)R^2]Co_2(CO)_5PPh_3$ (**2**) with diastereomeric excesses (% de) ranging from 10 to >95%. The isomeric complexes can be separated chromatographically and exhibit significant configurational stability, isomerizing only over a period of days at room temperature. The relative stereochemistry of the major isomer **2b** (R^1 = H, R^2 = Ph) has been established by X-ray diffraction.

The lure of cluster-promoted asymmetric reactions and catalysis has stimulated interest in the preparation and properties of chiral cluster complexes.[1] However, prospects for achieving this goal have dimmed somewhat with the appearance of recent reports of several chiral tetranuclear $MM'C_2$ and $M_2M'C$ and pentanuclear $M_2M'C_2$ clusters which racemize on the NMR time scale.[1-4] An exception has been found recently in the case of some diastereomeric (μ-acyl)trisomium clusters[5] which equili-

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[†] Address correspondence regarding the X-ray diffraction results to this author.

(1) Reviews: McGlinchey, M. J.; Mlekuz, M.; Bougeard, P.; Sayer, B. G.; Marinetti, A.; Saillard, J.-Y.; Jaouen, G. *Can. J. Chem.* **1983**, *61*, 1319. Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169.

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(3) Sutin, K. A.; Kolis, J. W.; Mlikuz, M.; Bougeard, P.; Sayer, B. G.; Quilliam, M. A., Faggiani, R.; Lock, C. J. L.; McGlinchey, M. J.; Jaouen, G. *Organometallics* **1987**, *6*, 439.

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Table I. Preparation of Diastereomeric $[(R^1C{\equiv}CCH(OH)R_2)Co_2(CO)_5(PPh_3)]$ (2) via Eq 1

compd	R^1	R^2	yield,[a] %	% de[b]
2a, **2a′**	H	Me	87	80
2b, **2b′**	H	Ph	93	60
2c	H	Bu^t	84	>95
2d, **2d′**	Ph	Me	99	10
2e	Ph	Pr^i	92	>95

[a] Yield after chromatography. [b] % de = % major isomer − % minor isomer.

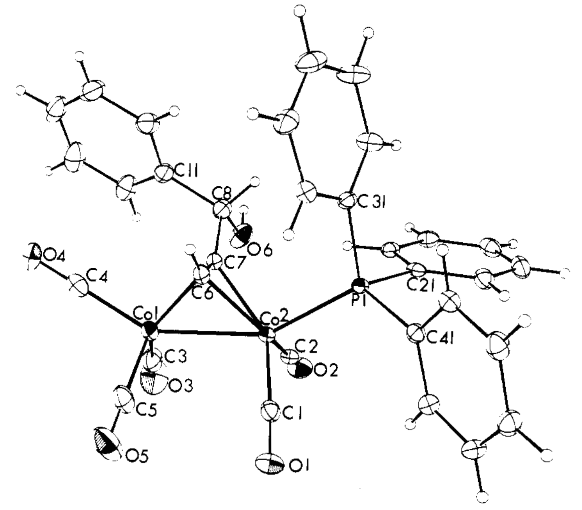
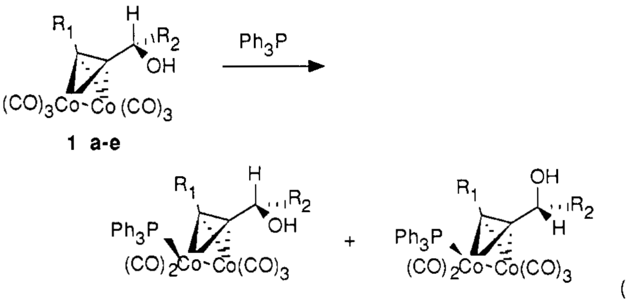


Figure 1. Molecular structure of **2b**. Selected bond lengths (Å): Co(1)–Co(2), 2.489 (1); Co(1)–C(3), 1.811 (2); Co(1)–C(4), 1.803 (2); Co(1)–C(5), 1.815 (2); Co(1)–C(6), 1.964 (2); Co(1)–C(7), 1.992 (2); Co(2)–P(1), 2.221 (1); Co(2)–C(1), 1.797 (2); Co(2)–C(2), 1.804 (2); Co(2)–C(6), 1.956 (2); Co(2)–C(7), 1.940 (2); C(6)–C(7), 1.330 (2). Selected bond angles (deg): C(3)–Co(1)–C(4), 101.5 (1); C(3)–Co(1)–C(5), 106.8 (1); C(4)–Co(1)–C(5), 99.1 (1); P(1)–Co(2)–Co(1), 149.6 (1); P(1)–Co(2)–C(2), 100.0 (1); C(1)–Co(2)–C(2), 105.9 (1); C(6)–C(7)–C(8), 142.3 (2); C(7)–C(6)–H(6), 139 (1).

brate over several minutes at 96 °C. As part of an effort to develop asymmetric coupling reactions of the synthetically versatile $(propargylium)Co_2(CO)_6{}^+Z^-$ complexes,[6] we became interested in the $(R^1C{\equiv}CCR^2R^3OH)Co_2(CO)_5L$ derivatives **2** which should exist as diastereomers because of the presence of a chiral cluster core and an asymmetric center on the side chain. We report herein: (a) that the preparation of **2** from $(R^1C{\equiv}CCR^2R^3OH)Co_2(CO)_6$ (**1**) proceeds in some cases with a high degree of stereoselectivity; and (b) that the diastereomers exhibit considerable configurational stability allowing their separation and structural characterization.

Dropwise addition of a solution of PPh_3 (0.8 equiv.) in 1:2 Et_2O/THF to a warmed (50 °C) solution of the hexacarbonyl complexes **1a–e** in the same solvent produced the monosubstituted derivatives **2** in excellent yield as dark red crystalline compounds (eq 1, Table I) accompanied by small amounts of the bis(phosphine) complexes $(R^1C{\equiv}CCR^2R^3OH)Co_2(CO)_4(PPh_3)_2$. ^1H NMR analysis of the crude products from **1a**, **1b**, and **1d** revealed the presence of two diastereomers[7] which could be separated easily by flash chromatography over silica (1:4 Et_2O/pentane) with little change in the isomer ratios. Only a single isomer was formed from **1c** and **1e**. In all cases the major isomer eluted first, followed by the bis(phosphine) complex **4** and then the minor (′) isomer (if present).[8] In order to establish the relative stereochemistry of one compound for correlation purposes, an X-ray structure determination was carried out on the major isomer **2b**.[9] Figure 1 reveals the typical pseudotetrahedral Co_2C_2 core found in (alkyne)-$Co_2(CO)_{6-n}L_n$ complexes[10] with the PPh_3 ligand occupying



(1)

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[6] Nicholas, K. M. *Acc. Chem. Res.* **1987**, *20*, 207.

[7] The presence of diastereomers was apparent from the presence of pairs of resonances for the C*H*OH protons (for **2a**/**2a′**, **2b**/**2b′**, **2d**/**2d′**) and the CH_3 protons for **2a**/**2a′** and **2d**/**2d′**; see ref 8 for complete spectroscopic data.

[8] Compound **2a**: mp 45–46 °C; IR (hexane) 2060, 2010, 2000 cm^{-1}; ^1H NMR (300 MHz, CS_2/C_6D_6) δ 7.15–7.34 (m, 15 H), 4.85 (d, 1 H, J_{H-P} = 2.4 Hz), 3.80 (dt, 1 H, J = 5.4, 6.9 Hz), 1.12 (d, 1 H, J = 6.9 Hz), 0.95 (d, 3 H, J = 5.6 Hz); $^{31}P\ \{^1H\}$ NMR (121.4 MHz, CD_3COCD_3, H_3PO_4) δ 54.0; MS (FAB, 70 eV), *m/e* 590 (M^+, 1), 534 (M^+ − 2CO, 11), 506 (M^+ − 3CO, 23), 478 (M^+ − 4CO, 48), 450 (M^+ − 5CO, 100). Anal. Calcd for $C_{27}H_{11}O_6Co_2P$: C, 54.92; H, 3.56; P, 5.25. Found: C 54.70; H, 3.61; P, 4.75. Compound **2a′**: mp 87–88 °C; IR (hexane) 2060, 2010, 2000 cm^{-1}; ^1H NMR (300 MHz, CS_2/C_6D_6) δ 7.1–7.4 (m, 15 H), 4.96 (d, 1 H, J = 4.5 Hz), 3.83 (m, 1 H), 1.14 (d + s, 4 H, J = 6.3 Hz); $^{31}P\ \{^1H\}$ NMR (121.4 MHz, CD_3COCD_3, H_3PO_4) δ 53.4; MS (FAB, 70 eV), *m/e* 590 (M^+, 1), 534 (M^+ − 2CO, 12), 506 (M^+ − 3CO, 46), 478 (M^+ − 4CO, 59), 450 (M^+ − 5CO, 100). Anal. Calcd for $C_{27}H_{11}O_6Co_2P$: C, 54.92; H, 3.56; P, 5.25. Found: C 55.82; H, 3.91; P, 4.58. Compound **2b**: mp 144–146 °C; IR (hexane) 2065, 2020, 2005 cm^{-1}; ^1H NMR (300 MHz, CS_2/C_6D_6) δ 7.25–7.48 (m, 15 H), 6.72–6.97 (m, 5 H), 4.89 (d, 1 H, J_{HP} = 1.8 Hz), 4.70 (d, 1 H, J = 5.4 Hz), 1.77 (d, 1 H, J = 5.4 Hz); $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_3COCD_3, H_3PO_4) δ 54.5; MS (FAB, 70 eV), m/e 652 (M^+, 1), 624 (M^+ − CO, 1), 596 (M^+ − 2CO, 9), 568 (M^+ − 3CO, 12), 540 (M^+ − 4CO, 20), 512 (M^+ − 5CO, 100). Anal. Calcd for $C_{32}H_{23}O_6Co_2P$: C, 58.91; H, 3.55; P, 4.75. Found: C, 59.68; H, 3.81; 4.83. Compound **2b′**: mp 171–174 °C; IR (hexane) 2060, 2010, 1995 cm^{-1}; ^1H NMR (300 MHz, CS_2/C_6D_6) δ 7.01–7.39 (m, 20 H), 5.09 (d, 1 H, J = 6 Hz), 5.00 (s, 1 H), 1.32 (d, 1 H, J = 6 Hz); $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_3COCD_3, H_3PO_4) δ 53.4; MS (FAB, 70 eV), *m/e* 624 (M^+ − CO, 1), 596 (M^+ − 2CO, 5), 568 (M^+ − 3CO, 13), 540 (M^+ − 4CO, 20), 512 (M^+ − 5CO, 100). Compound **2c**: mp 115–119 °C; IR (thin film) 2020, 1990, 1950 (sh) cm^{-1}; ^1H NMR (300 MHz, CS_2/C_6D_6) δ 7.1–7.4 (m, 15 H), 5.02 (d, 1 H, J_{HP} = 1.8 Hz), 3.4 (d, 1 H, J = 7 Hze, 1.4 (d, 1 H, J = 7 Hz), 0.57 (s, J = 9 Hz); $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_3COCD_3, H_3PO_4) δ 54.0; MS (FAB, 70 eV), *m/e* 576 (M^+ − 2CO, 9), 548 (M^+ − 3CO, 16), 520 (M^+ − 4CO, 51), 492 (M^+ − 5CO, 100). Compound **2d**: mp 33–35 °C; IR (CCl_4) 2010, 1985, 1945^{-1}; ^1H NMR (300 MHz, CS_2/C_6D_6) δ 6.93–7.16 (m, 20 H), 4.06 (dq, 1 H, J = 3,6 Hz, 1.23 (d, 1 H, J = 3 Hz), 1.15 (d, 3 H, J = 6 Hz); $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_3COCD_3, H_3PO_4) δ 50.0; MS (FAB, 70 eV), *m/e* 610 (M^+ − 2CO, 15), 582 (M^+ − 3CO, 14), 555 (M^+ − 4CO, 16), 526 (M^+ − 5CO, 100). Anal. Calcd for $C_{33}H_{25}O_6Co_2P$: C, 59.48; H, 3.78; P, 4.63. Found: C, 59.77; H, 3.75; P, 4.52. Compound **2d′**: IR (hexane) 2005, 1990, 1940; ^1H NMR (300 MHz, CS_2/C_6D_6) δ 7.0–7.2 (m, 20 H), 4.02 (dq, 1 H, J = 3.5,5 Hz), 1.12 (d, 3 H, J = 5 Hz), 1.09 (d, 1 H, J = 3.5 Hz); $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_3COCD_3, H_3PO_4) δ 50.0; MS (FAB, 70 eV), *m/e* 610 (M^+ − 2CO, 3), 582 (M^+ − 3CO, 2), 554 (M^+ − 4CO, 27), 526 (M^+ − 5CO, 93), 397 (100). Compound **2e**: IR (CCl_4) 2065, 2010, 1935 cm^{-1}; ^1H NMR (300 MHz, CS_2/C_6D_6) δ 6.92–7.23 (m, 20 H), 3.20 (m, 1 H), 1.39 (m, 1 H), 1.20 (d, 1 H, J = 6.3 Hz), 0.87 (d, 3 II, J = 6.6 Hz), 0.54 (d, 3 H, 6.6 Hz); $^{31}P\ \{H\}$ NMR (121.4 MHz, CD_3COCD_3, H_3PO_4) δ 49.1; MS (FAB, 70 eV), *m/e* 667 (M^+ − CO, 10), 638 (M^+ − 2CO, 23), 610 (M^+ − 3CO, 6), 582 (M^+ − 4CO, 69), 554 (M^+ − 5CO, 100). Anal. Calcd for $C_{35}H_{24}O_6Co_2P$: C, 60.53; H, 4.21; P, 4.46. Found: C, 59.63; H, 4.20; P, 4.85.

[9] X-ray crystal data for **2b**: mol formula $C_{32}H_{23}Co_2O_6P_1$; M_r 652.37; triclinic space group $P\bar{1}$, a = 9.089 (4) Å, b = 10.110 (2) Å, c = 15.350 (4) Å, α = 92.64 (2)°, β = 96.97 (2)°, γ = 92.11 (2)°; V = 1397.3 Å^3; Z = 2; D_{calcd} = 1.550 g cm^3; $F(000)$ = 664; $\lambda(Mo\ K_\alpha)$ = 0.7107 Å, $\mu(Mo\ K_\alpha)$ = 12.2 cm^{-1}. Cell dimensions and intensities of 4879 reflections were measured at 160 ± 2 K ($2\theta_{max}$ = 50°; $\pm h, \pm k, l$) on an Enraf-Nonius CAD-4 diffractometer. The structure was solved by the heavy-atom method and refined anisotropically by a full-matrix least-squares method (hydrogen atoms were refined isotropically). All calculations were carried out by using the SHELX-76 program. For 4182 unique observed reflections [$I > 2\sigma(I)$] the final R = 0.023, R_w = 0.033, and ρ_{max} in the final difference map = 0.4 e Å^{-3}.

[10] Cotton, F. A.; Jamerson, J. D.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 1774. Sly, W. G. *Ibid.* **1959**, *81*, 18. Gregson, D.; Howard, J. A. K. *Acta Crystallogr., Sect. C* **1983**, *C39*, 1024. Saha, M.; Muchmore, S.; van der Helm, D.; Nicholas, K. M. *J. Org. Chem.* **1986**, *51*, 1960.

an axial position, trans to the Co–Co bond. Such is generally the case with $(Q_2)Co_2(CO)_4L_2$ derivatives,[11] but this is the first $n = 1$ example. The stereochemistry at the asymmetric C1 and C2 centers is seen to be (*S*,*R*)[12] with the large Ph group on C1 directed away from the bulky PPh_3 ligand. The same stereochemistry is assigned to the major (or exclusive) isomers **2a,c** and **2d,e** on the basis of their chromatographic elution behavior.

In the course of characterizing complexes **2a–e** the minor isomers **2a′,b′,d′** were found to isomerize and disproportionate very slowly in solution at 20 °C ($t_{1/2}$ = ca. 50–200 h) to produce mixtures containing the major isomer, the bis(phosphine)complexes **4a,b,d**, and the starting hexacarbonyl complexes **1a,b,d** (eq 2). Formation of the dis-

$$\mathbf{2a',b',d'} \rightarrow \mathbf{2a,b,d} + \mathbf{4a,b,d} + \mathbf{1a,b,d} + \text{decomposition} \tag{2}$$

proportionated products in eq 2 suggests that PPh_3 dissociation/readdition may be involved in both the isomerization and the disproportionation mechanisms. This hypothesis was further supported by the results of a crossover experiment involving isomerization of **2b′** in the presence of $(Me_3SiC{\equiv}CH)Co_2(CO)_6$ monitored by ^1H NMR. Thus, formation of the major isomer **2b** was found to be accompanied by a substantial amount of the crossover product $(Me_3SiC{\equiv}CH)Co_2(CO)_5(PPh_3)$[13] as well as the disproportionation products (eq 3). An alternative

$$\mathbf{2b'} + (Me_3SiC{\equiv}CH)Co_2(CO)_6 \rightarrow \mathbf{2b} + (Me_3SiC{\equiv}CH)Co_2(CO)_5(PPh_3) \tag{3}$$

isomerization pathway involving racemization at C1 via OH^- (or H_2O) dissociation/reassociation (facilitated by the considerable stability of the $(propynyl)Co_2(CO)_5(PPh_3)^+$ species[14]) is less likely because the isomerization of **2b′** in MeOH failed to produce any of the corresponding methyl ether(s) and its rate of isomerization was similar in solvents a differing polarity, i.e. benzene, THF, MeOH, ether, and hexane. Other *intramolecular* isomerization mechanisms such as an "acetylene twist"[15] or other cluster skeletal rearrangements[1,2] cannot be excluded at present and await future investigations.

The configurational stability of **2a–e** was unexpected given the facile racemization of the related tetrahedral cluster compounds[16] $(PhC{\equiv}CCO_2Pr^i)[CpNiML_n]$ (ML_n = $Co(CO)_3$, $CpMo(CO)_2$),[2] and $Pr^iO_2CCo_3(CO)_7L_2$[2,3]). The magnitude of the diastereoselectivity observed in the **1** → **2** conversion is is also surprising, and its origin is not apparent. There is some correlation with the steric demand of the R^2 group (Table I), the isopropyl and *tert*-butyl derivatives giving only one isomer. Control experiments (at 50 °C) indicate that *partial* isomerization occurs under the reaction conditions so that the observed % de's are neither truly kinetic nor thermodynamic in origin. Nonetheless, exploitation of this novel type of asymmetric induction in effecting stereocontrolled coupling reactions of the extremely stable propargylium complexes derived from protonation of **2a–e**[14] appears very promising. Results toward this end will be reported in forthcoming publications.[17]

Acknowledgment. We are grateful for support provided by the National Institutes of Health (GM 34799) and for a gift of cobalt carbonyl from Pressure Chemical Co.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond lengths and bond angles (8 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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[11] Bonnett, J.-J.; Mathieu, R. *Inorg. Chem.* **1978**, *17*, 1973. Bianchini, C.; Dapporto, P.; Meli, A. *J. Organomet. Chem.* **1979**, *174*, 205. Bird, P. H.; Fraser, A. R.; Hall, D. N. *Inorg. Chem.* **1977**, *16*, 1923.

[12] Other enantiomer, (*R*,*S*), present in unit cell is not shown.

[13] ^1H NMR (300 MHz, C_6D_6) of $(Me_3SiC{\equiv}CH)Co_2(CO)_5(PPh_3)$: δ 7.19–7.32 (m, 15 H), 5.30 (d, 1 H, *J* = 7 Hz), 0.01 (s, 9 H); verified by independent synthesis from $(Me_3SiC{\equiv}CH)Co_2(CO)_6$ + PPh_3.

[14] Bradley/Nicholas unpublished results.

[15] These cluster complexes racemize between ca. 250 and 380 K *on the NMR time scale* with estimated ΔG = 13–21 kcal/mol. Assuming typical rate dependency on *T* and a first-order process for isomerization, complexes **2** are crudely estimated to racemize ca. 10^{-5} times more slowly that the former.

[16] Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858.

[17] **Note Added in Proof.** After submission of this paper, the preparation of diastereomeric $(PhC{\equiv}CH)Co_2(CO)_5(^*PR_3)$ containing an optically active phosphine was reported. Isomerization of this complex occurs in ca. 3 h at 60 °C. Bladon, P.; Pauson, P. L.; Brunner, H.; Eder, R. *J. Organomet. Chem.* **1988**, *355*, 499.

Photochemical Conversion of (η^1-Butadienyl)iron Complexes to Hydroxyferrocenes[1]

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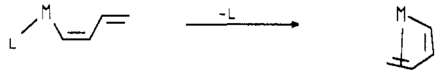
Summary: The photolysis of $(\eta^5\text{-}C_5H_5)(CO)_2Fe(\eta^1\text{-buta-1,3-dienyl})$ complexes gave substituted hydroxyferrocenes in high yields. Low-temperature ^1H NMR and IR studies implicate loss of CO as the sole photochemical process with an η^3-butadienyl complex and an η^5-pentadienoyl complex as key intermediates in this rearrangement.

We have recently been interested in utilizing η^1-butadienyl complexes as potential synthons of transition metallacycles.[2] The corresponding η^3-butadienyl complexes **1**, which may be approached with loss of a ligand from η^1-butadienyl complexes (eq 1), are of further interest due to their intrinsically novel bonding and reactivity.[3,4] We here report a detailed study of the synthesis and conversion of $(\eta^5\text{-}C_5H_5)(CO)_2Fe(\eta^1\text{-buta-1,3-dienyl})$ complexes to thermodynamically unstable η^3-butadienyl complexes. These complexes undergo nearly quantitative conversion



(1)

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[1] (a) Initial work was presented at the 192nd National Meeting of the American Chemical Society, Anaheim, CA, Sept 1986; paper INOR 263 (Neil T. Allison, Warunee Yongkulrote, H. D. Frame III, C. Mike, and B. Durham). (b) Initial results: Yongskulrote, W. Doctoral Dissertation, University of Arkansas, 1985.

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