Associative Stereomutation of a Pentacoordinate Transition-Metal Complex: Access to the Required Octahedral Intermediate through Stereoselective CO Uptake at an Unsaturated Ruthenium(II) Center

Gordon W. Bushnell, Miguel Angel Casado, and Stephen R. Stobart*

Department of Chemistry, University of Victoria, British Columbia, Canada V8W 2Y2

Received November 8, 2000

*Summary: Reaction of $SiH(Me)(CH_2CH_2CH_2PPh_2)_2$ (i.e. "biPSiH") with mer-$RuH(PPh_3)_3(CO)Cl$ affords the 5-coordinate Ru(II) monocarbonyl chloride Ru(biPSi)(CO)Cl (**1**), which adds CO to yield the 6-coordinate dicarbonyl analogue $Ru(biPSi)(CO)_2Cl$ (**2**). Stereoselective incorporation of ^{13}CO to give the labeled analogue **2*** shows that on subsequent heating in refluxing toluene **1** is regenerated as a mixture of syn and anti diastereomers (ca. 3:1 ratio).*

Predictive management of the differential rates that determine selectivity remains a priority objective in homogeneous catalysis.[1] Use of rational ligand design to control the interaction between a substrate and a reactive metal site depends on intelligent manipulation of both steric and electronic parameters, but what contribution is made by each of these to net binding or turnover characteristics in any particular situation is often very difficult to assess.[2] We show that the two influences are clearly distinguishable, however, during uptake and release of carbon monoxide at an unsaturated Ru(II) center that is held within a "biPSi" framework: thus, the latter, which is[3] a semirigid, electron-releasing, tridentate silyl ligand derived from the silane[4] $SiH(Me)(CH_2CH_2CH_2PPh_2)_2$ (i.e. "biPSiH"), is able to exert a singular degree of[5] stereoelectronic control. The same chemistry operates as a unique associative pathway for diastereoisomerization of a distorted 5-coordinate geometry ("dist TBP")[6] that is itself of major interest.

Addition of biPSiH to the known[7] mononuclear precursor *mer*-$RuH(PPh_3)_3(CO)Cl$ afforded a bright yellow, air-stable solid that reacted further on exposure to gaseous carbon monoxide, giving a white, air-stable adduct. On the basis of analytical and mass spectrometric data,[8] the two products were concluded to be the 5-coordinate Ru(II) monocarbonyl chloride Ru(biPSi)(CO)Cl (**1**; 70% isolated yield) and its 6-coordinate dicarbonyl analogue $Ru(biPSi)(CO)_2Cl$ (**2**; 95%), respec-

---

(1) Palucki, M.; Finney, N. S.; Pospisil, P. J.; Guler, M. L.; Ishida, T.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 948. van der Veen, L. A.; Boele, M. D. K.; Bregman, F. R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J.; Schenk, H.; Bo, C. *J. Am. Chem. Soc.* **1998**, *120*, 11616. Burk, M. J.; Allen, J. G.; Kiesman, W. F. *J. Am. Chem. Soc.* **1998**, *120*, 657. Trost, B. M.; Hildebrand, S.; Dogra, K. *J. Am. Chem. Soc.* **1999**, *121*, 10416. Collman, J. P.; Wang, Z.; Straumanis, A.; Quelquejeu, M.; Rose, E. *J. Am. Chem. Soc.* **1999**, *121*, 460. Deng, L.; Ziegler, T.; Woo, T. K.; Margl, P.; Fan, L. *Organometallics* **1998**, *17*, 3240. Bennani, Y.; Hanessian, S. *Chem. Rev.* **1997**, *97*, 3161. Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. See also Bosnich, B. *Acc. Chem. Research* **1998**, *31*, 667.

(2) Casey, C. P.; Paulsen, E. L.; Beuttenmueller, E. W.; Proft, B. R.; Petrovich, L. M.; Matter, B. A.; Powell, D. R. *J. Am. Chem. Soc.* **1999**, *121*, 63; and references therein. Gung, B. W.; le Noble, W. J. *Chem. Rev.* **1999**, *99*, 1067.

(3) Brost, R. D.; Bruce, G. C.; Joslin, F. L.; Stobart, S. R. *Organometallics* **1997**, *16*, 5669.

(4) Joslin, F. L.;. Stobart, S. R. *Inorg. Chem.* **1993**, *32*, 2221. Zhou, X.; Stobart, S. R.; Gossage, R. A. *Inorg. Chem.* **1997**, *36*, 3745.

(5) Albinati, A.; Bakhmutov, V. I.; Caulton, K. G.; Clot, E.; Eckert, J.; Eisenstein, O. Gusev, D. G.; Grushin, V. V.; Hauger, B. E.; Klooster, W. T.; Koetzle, T. F.; McMullan, R. K.; O'Loughlin, T. J.; Pelissier, M.; Ricci, R. S.; Sigalas, M. P.; Vymentis, A. B. *J. Am. Chem. Soc.* **1993**, *115*, 7300.

(6) Riehl, R.-F.; Jean, Y.; Eisenstein, O.; Pélissier, M. *Organometallics* **1992**, *11*, 729. Auburn, M. J.; Holmes-Smith, R. D.; Stobart, S. R.; Bakshi, P. K.; Cameron, T. S. *Organometallics* **1996**, *15*, 3032.

(7) James, B. R.; Markham, L. D.; Benjamin, C. H.; Rempel, G. L. *J. Chem. Soc., Dalton Trans.* **1973**, 2247. See also: Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 45.

(8) Addition of *mer*-$RuH(PPh_3)_3(CO)Cl$ (isolated as a very pale coffee-colored solid, single diastereomer, H trans to P) to a solution (benzene or toluene) of biPSiH (1.1 mol equiv) followed by heating to 60 °C is accompanied over 30 min by formation of a clear, bright yellow solution. After the mixture was stirred for 3 h, removal of the solvent in vacuo leads to recovery of a yellow oil, which when washed with hexanes precipitates a solid residue; on further washing with methanol compound **1** may be recovered as a bright yellow, air-stable solid. Redissolution of the latter in dichloromethane and then either (a) bubbling a rapid stream of CO gas through the reaction mixture or, more conveniently, (b) stirring the solution (30 min) under CO gas (1 atm) results in rapid discharge of the yellow color; after concentration to ca. 15% of the original volume, addition of hexanes precipitates compound **2** as a white, air-stable solid. Suitable single crystals of **1** and **2** (methylene chloride monosolvate) were obtained by slow deposition from solutions in CH_2Cl_2/hexanes. Data for compound **1** (syn diastereomer, **1-s**) are as follows. Anal. Calcd for $C_{32}H_{35}ClOP_2RuSi$: C, 58.04; H, 5.33. Found: C, 57.97; H, 5.27. ^{1}H NMR (C_6D_6, 360.1 MHz): δ 6.88−8.04 (m, 20H, PPh_2), 2.21 (m, 4H, CH_2), 1.99 (m, 2H, CH_2), 1.61 (m, 2H, CH_2), 1.09 (s, 3H, CH_3), 1.00 (m, 4H, CH_2). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 145.8 MHz): δ 17.6 (s). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 90.6 MHz): δ 201.2 (t, CO, $^{2}J_{P-CO} = 13.4$ Hz), 135.0−127.2 (PPh_2), 30.8 (t, PCH_2, $^{1}J_{P-C} = 15.6$ Hz), 21.5 (s, $SiCH_2CH_2$), 19.2 (s, $SiCH_2$), 5.4 (s, CH_3). $^{29}Si\{^{1}H\}$ NMR (C_6D_6, 49.7 MHz): δ 53.7 (t, $^{2}J_{P-Si} = 12.8$ Hz). IR (KBr pellet): ν(CO) 1911 cm^{-1}. Data for compound **2** are as follows. Anal. Calcd for $C_{33}H_{35}ClO_2P_2RuSi$: C, 57.42; H, 5.11. Found: C, 57.10; H, 5.00. ^{1}H NMR: δ 6.84−8.05 (m, 20H, PPh_2), 2.34 (m, 2H, CH_2), 2.00 (m, 2H, CH_2), 1.89 (m, 4H, CH_2), 1.86 (s, 2H, CH_2), 1.78 (m, 2H, CH_2), 0.40 (s, CH_3). $^{31}P\{^{1}H\}$ NMR: δ 14.7 (s). $^{13}C\{^{1}H\}$ NMR: δ 202.4 (t, CO_{anti}, $^{2}J_{P-CO} = 14.6$ Hz), 196.8 (t, CO_{syn}, $^{2}J_{P-CO} = 12.2$ Hz), 19.1 (s, $SiCH_2$), 20.7 (s, $SiCH_2CH_2$), 32.5 (t, PCH_2, $^{1}J_{P-C} = 15.8$ Hz), 6.9 (s, CH_3). $^{29}Si\{^{1}H\}$ NMR: δ 10.9 (t, $^{2}J_{P-Si} = 11.0$ Hz). IR: ν(CO) 2047 (w), 1944 (s) cm^{-1}. Crystal data for **1-s**: $C_{32}H_{35}ClOP_2RuSi$, $M_r = 662.18$, triclinic, $P\bar{1}$ (No. 2), $a = 9.459(3)$ Å, $b = 12.106(3)$ Å, $c = 14.367(7)$ Å, $\alpha = 100.31(3)°$, $\beta = 98.47(3)°$, $\gamma = 102.50(2)°$, $V = 1550.3$ Å^3, $Z = 2$, $\rho_{calcd} = 1.419$ g cm^{-3}, $F(000) = 680$, $\lambda = 0.710\ 69$ Å, $T = 293$ K, μ(Mo Kα) = 7.447 cm^{-1}, 4024 unique reflections, 2112 observed reflections refined to a final $R = 0.0648$, $R_w = 0.0789$. Crystal data for **2**: $C_{33}H_{35}ClO_2P_2RuSi\cdot CH_2Cl_2$, $M_r = 775.13$, orthorhombic, $Pbn2_1$ (setting of No. 33), $a = 9.754(4)$ Å, $b = 21.658(7)$ Å, $c = 33.311(14)$ Å, $V = 7037(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.463$ g cm^{-3}, $F(000) = 3168$, $\lambda = 0.710\ 69$ Å, $T = 293$ K, μ(Mo Kα) = 8.181 cm^{-1}, 6319 unique reflections, 4181 observed reflections refined to a final $R = 0.0785$, $R_w = 0.0980$. Thermal motion of the methylene chloride solvent molecules contributed significantly to the relatively high R factor for **2**, while because of the crystal dimensions a valid improvement in either data set was considered to be unlikely through application of an absorption correction. Further details are included in the Supporting Information.

10.1021/om0009482 CCC: \$20.00
Publication on Web 01/26/2001

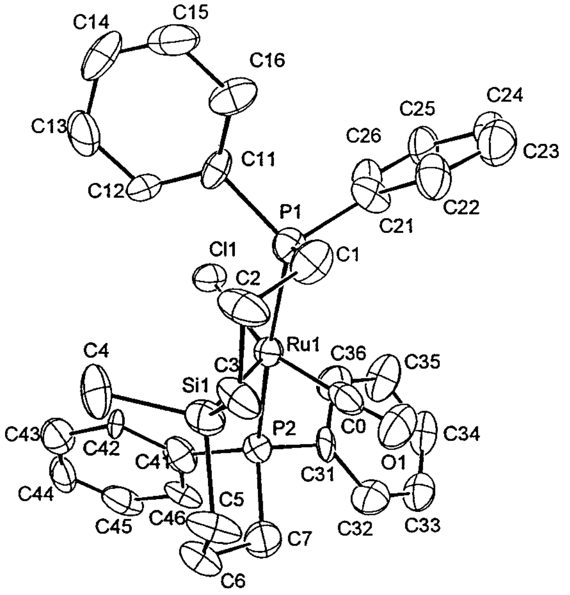
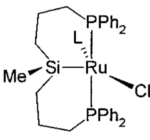
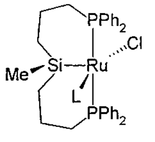


Figure 1. Molecular geometry of complex **1** (syn diastereomer, i.e. **1-s**). Selected bond lengths (Å) and angles (deg): Ru−Cl, 2.414(4); Ru−P(1), 2.366(5); Ru−P(2), 2.371(5); Ru−Si, 2.339(5); Ru−C, 1.80(2); P(1)−Ru−P(2), 175.8(2); Si−Ru−C, 80.1(6); Si−Ru−Cl, 122.9(2); C−Ru−Cl, 157.1(6); Cl−Ru−P(1), 90.9(2); Cl−Ru−P(2), 89.2(2); Si−Ru−P(1), 91.5(2); Si−Ru−P(2), 90.1(2).

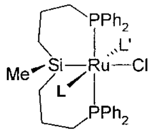
tively; this was confirmed by using X-ray crystallography to establish the molecular structure of each of the new complexes.[8] The monocarbonyl adopts a severely distorted trigonal-bipyramidal (dist TBP) geometry (Figure 1), in which although coordination of Ru by the P atoms of the biPSi cage is regularly coaxial, all three equatorial angles are different from each other and from 120°; the Cl atom (attached to Ru) is adjacent to the biPSi Me group (at Si) of what is thus[3] referred to as the syn diastereomer **1-s**. The CO adduct **2** of **1** is unambiguously characterized as a trans dicarbonyl (Figure 2); the unit cell contains two independent molecules that differ from one another only in the conformational relationship of the biPSi methylene backbones, a situation like that found in crystalline *cis*-Os(CO)$_2$(chel)$_2$ (chel = PPh$_2$CH$_2$CH$_2$SiMe$_2$−), where skew and parallel dispositions of the pairs of simple chelate units coexist.[9]



(1-s, L = CO)
(1-s*, L = ^{13}CO)



(1-a, L = CO)
(1-a*, L = ^{13}CO)



(2, L = L' = CO)
(2^{syn*}, L = ^{13}CO, L' = CO)
(2^{anti*}, L = CO, L' = ^{13}CO)
(2$^{syn-anti*}$, L = L' = ^{13}CO)

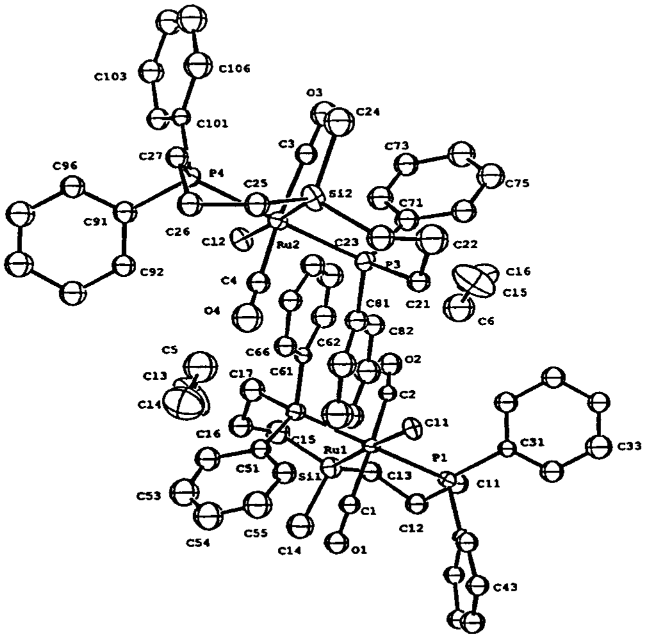
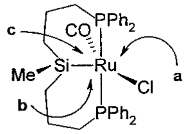


Figure 2. Molecular geometry of complex **2**. Selected bond lengths (Å) and angles (deg): Ru(1)−Cl(1), 2.547(6); Ru(1)−P(1), 2.366(7); Ru(1)−P(2), 2.384(8); Ru(1)−Si(1), 2.417(7); Ru(1)−C(1), 1.88(3); Ru(1)−C(2), 1.95(2); P(1)−Ru(1)−P(2), 176.5(2); Si(1)−Ru(1)−C(1), 83.7(8); Si(1)−Ru(1)−C(2), 81.0(7); Si(1)−Ru(1)−Cl(1), 174.5(3); C(1)−Ru(1)−C(2), 164.3(10); Cl(1)−Ru(1)−C(1), 90.8(8); Cl(1)−Ru(1)−C(2), 104.5(7); Cl(1)−Ru(1)−P(1), 89.3(2); Cl(1)−Ru(1)−P(2), 87.4(2); Si(1)−Ru(1)−P(1), 91.4(3); Si(1)−Ru(1)−P(2), 91.8(3). Note the difference in conformation (skew vs parallel) of the methylene backbones P(1)−C(11)−C(12)−C(13)−Si(1)−C(15)−C(16)−C(17)−P(2) vs P(3)−C(21)−C(22)−C(23)−Si(2)−C(25)−C(26)−C(27)−P(4).

Treatment of solutions of yellow **1-s** with ^{13}CO gas (99% atom purity, <0.8 atm, 295 K) afforded a colorless isotopomer of **2**, Ru(biPSi)(CO)(^{13}CO)Cl (**2***). Exposure of **2** (in benzene or toluene solution) to ^{13}CO gas under ambient conditions led to rapid exchange to yield the same isotopomer **2***. Examination of this product using ^{13}C NMR revealed that the label had been incorporated into only one site of **2** (that for which δ_{CO} is 196.8 ppm): i.e., consistent with stereoselective entry (or exchange) along trajectory **I$_b$** into the syn site of **1**, giving **2^{syn*}** (rather than into the widest angle, that trans to Si, along **I$_a$**, or the narrowest, **I$_c$**, either of which would afford a *cis*-dicarbonyl geometry). When this isotopomer was refluxed in toluene, a yellow color was regenerated that gradually deepened over 3 h, so that after concentration and then addition of hexanes a yellow solid was recovered. This was shown analytically to be the monocarbonyl species and by NMR to be predominantly syn, formed as a mixture of unlabeled **1-s** and its ^{13}CO-labeled isotopomer **1-s***, which was accompanied, however, by a minor proportion (ca. 1:3) of a second diastereomer. From the effect of ^{13}C incorporation it is evident from the NMR data[10] that this can only be the



I

---

(9) Holmes-Smith, R. D.; Stobart, S. R.; Vefghi, R.; Zaworotko, M. J.; Jochem, K.; Cameron, T. S. *J. Chem. Soc., Dalton Trans.* **1987**, 969.

(10) Data for **1-a** are as follows. ^{1}H NMR: δ 6.90−7.80 (m, 20H, PPh$_2$), 2.90 (m, 2H, CH_2), 2.22 (m, 4H, CH_2), 1.80 (m, 2H, CH_2), 1.18 (s, 2H, CH_2), 0.85 (m, 2H, CH_2), 0.40 (s, 3H, CH_3). ^{31}P{^{1}H} NMR: δ 24.6 (s). ^{13}C{^{1}H} NMR: δ 200.7 (t, *C*O, $^2J_{P-CO}$ = 13.3 Hz), 134.8−127.4 (PPh$_2$), 27.4 (t, P*C*H$_2$, $^1J_{P-C}$ = 15.4 Hz), 23.0 (s, SiCH$_2$*C*H$_2$), 19.7 (s, Si*C*H$_2$), 1.0 (s, *C*H$_3$). ^{29}Si{^{1}H} NMR: δ 65.8 (t, $^2J_{P-Si}$ = 13.5 Hz). IR: ν(CO) 1920 cm^{-1}.

anti correspondent of **1-s**, again formed as[11] an isotopomeric mixture, i.e. with label present (**1-a***) or not (**1-a**): coupling between mutually cis ^{13}C and ^{31}P nuclei leads to diagnostic triplets (attributable to δ_{CO} of **1-s***, **1-a***; $^{2}J_{PC} \approx 13$ Hz) in a ratio that is echoed through the two[10] mutually shifted but otherwise very similar sets of ^{13}C resonances due to biPSi skeletal carbon atoms. In contrast, reflux (toluene) of pure **1-s** did not result in detection (by ^{31}P NMR) of any **1-a**, nor was there any change in the **1-s**:**1-a** ratio on heating solutions containing both. Exposure of the latter to ^{13}CO gas was accompanied by immediate formation of the trans dicarbonyl **2** showing the label in anti as well as syn CO sites, (i.e., of $\mathbf{2}^{\mathbf{anti}*}$ *and* $\mathbf{2}^{\mathbf{syn}*}$) and more particularly indicating (by observation of $^{2}J_{CC(trans)}$) the formation of the "double label" isotopomer Ru(biPSi)(^{13}CO)$_2$Cl ($\mathbf{2}^{\mathbf{anti}*-\mathbf{syn}*}$). Subsequent exposure of these solutions to unlabeled CO led to rapid loss of label but from the syn site only.

Reaction of the saturated Ru(II) precursor *mer*-RuH(PPh$_3$)$_3$(CO)Cl with biPSiH to afford the unsaturated complex **1-s** as the only isolated product is itself unusual, implicating a Ru(IV) intermediate having a *cis*-dihydrido geometry to accommodate H$_2$ elimination,[12] suggesting that associative interaction of **1** with H$_2$ may be kinetically accessible, and implying a high degree of selectivity in the required sequence of addition/elimination steps. The solid-state geometry of **1-s** represents a significant anomaly, since virtually all crystallographically characterized Ru(II) analogues are[13] unambiguously recognizable as square pyramidal (SQP) and have been predicted[14] on the basis of MO calculations to be so. Extrapolating from the calculated potential energy surface for[15] RuH(PH$_3$)$_2$(CO)Cl (**3**), the structure of **1-s** (Figure 1; i.e. in which the angles defined[15] as α and β are respectively 122 and 79°) would be viewed as occupying a position partway along a shallow energy gradient connecting regular SQP configurations with Si or CO apical (corresponding to T_H, T_{CO} of **3**) and strongly stabilized vs a SQP with Cl apical (T_{Cl}): it offers three distinguishable approaches (**I**: **a**−**c**) for CO addition. The narrow Si−Ru−CO angle (<80°) and the Si−Ru bond length, which at 2.338 Å is much shorter than that of 2.417 Å in **2** or 2.457 Å in[3] RuH(biPSi)(CO)$_2$, are even more exaggerated than corresponding structural features observed[16] for Os(SiMe$_3$)(PPh$_3$)$_2$(CO)Cl (which has a geometry close to regular SQP) and which have been interpreted as evidence for (weak) electronic interaction between CO and −SiR$_3$ as well as significant π-back-donation from Os onto the latter. Interestingly, the structure of 6-coordinate **2** shows a similar degree of bending of *both* CO groups toward Si, together with a Ru−Cl bond (mean 2.55 Å) much longer than that in **1-s** (2.421 Å), consistent with the expected "push−pull" π interaction[14,15,17] in the latter.

The absence of a 6-coordinate product arising from CO entry into the widest equatorial angle of **1-s** (see Figure 1 and **I-a**: i.e., into what Eisenstein, Caulton, et al. refer to[5,15] as the "obvious" site) signals that the ratio of binding to release rates k_{on}/k_{off} is too small to accommodate net CO uptake at a site that is trans to the strongly electron-releasing silyl fragment. Instead, the productive manifold is the only pathway to a *trans*-dicarbonyl geometry, **I-b**, affording the CO adduct **2**, which although it is isolable continues to exchange rapidly along **I-b** (but *not* **I-c**). This is the clearest evidence yet that the strong and directed electronic influence[3,6] of a silyl group can be used to control substrate binding at a reactive transition-metal center. Just as significantly, while from the experiments described above it is not possible to compare directly the "on" rates for formation of the dicarbonyl **2** from frontside (syn) approach to **1-s** vs backside (anti) approach to **1-a**, it is apparent from the temperature regime required to produce the latter from **2** that CO release on the syn face must be at least 10^3 faster than from the anti.[18] These two binding sites are subject to nominally identical electronic influences, so that such "face discrimination" may be ascribed explicitly to the spatial contour of the biPSi framework: this is an unusually simple example of kinetic control that is attributable only to the steric profile of a ligand assembly, a prominent theme in discussions[1,2] of stereoselective substrate binding and catalysis.

We conclude by stressing that along the **1-s**−**2**−**1-a** manifold, access to an octahedral configuration is providing an *associative* pathway for stereomutation of a pentacoordinate geometry that appears itself to be too rigid to undergo intramolecular reorganization (i.e. resembling S$_N$2 racemization of an optically active carbon center): this is effectively the antithesis of a fundamental mechanistic premise in transition-metal chemistry, that permutation of a rigid octahedral structure is likely to occur *dissociatively* through a stereochemically nonrigid unsaturated state.

Acknowledgment. Funding for this research from the NSERC of Canada is gratefully acknowledged.

Supporting Information Available: Tables giving full crystallographic details, positional and thermal parameters, and bond distances and angles for compounds **1-s** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0009482

---

(11) The ^{31}P resonances for the two diastereomers (i.e. at δ 17.6 for **1-s** and at δ 24.6 for **1-a**) show isotope shifts that at 145.8 MHz are only just resolved but suggest that in the overall product distribution the **1-a***/**1-a** ratio (at ca. 1:1) is larger than **1-s***/**1-s** (ca. 3:7).

(12) Use of ^{1}H NMR spectroscopy to monitor the reaction in situ provided no evidence for any intermediate hydride complexes, but a singlet resonance that accumulated at δ 4.25 is attributable to formation of molecular H$_2$.

(13) Ferrando, G.; Caulton, K. G. *Inorg. Chem.* **1999**, *38*, 4168. Huang, D.; Streib, W. E.; Bollinger, J. C.; Caulton, K. G.; Winter, R. F.; Scheiring, T. *J. Am. Chem. Soc.* **1999**, *121*, 8087. Exceptions include those described in the following: Skapski, A. C.; Troughton, P. G. H. *Chem. Commun.* **1968**, 1230. Chin, B.; Lough, A. J.; Morris, R. H.; Schweitzer, C. T.; D'Agostino, C. *Inorg. Chem.* **1994**, *33*, 6278.

(14) Heyn, R. H.; Macgregor, S. A.; Nadasdi, T. T.; Ogasawara, M.; Eisenstein, O.; Caulton, K. G. *Inorg. Chim. Acta* **1997**, *259*, 5.

(15) Poulton, J. T.; Sigalas, M. P.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1993**, *32*, 5490.

(16) Hubler, K.; Hunt, P. A.; Maddock, S. M.; Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Schwerdtfeger, P.; Wright, L. J. *Organometallics* **1997**, *16*, 5076.

(17) Poulton, J. T.; Sigalas, M. P.; Folting, K.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 1476.

(18) We do not intend to imply by this statement that the *mechanism* of formation of **1a** from **2** is *necessarily* simple release of CO from the anti face (i.e. corresponding to the "off" step in the exchange of CO on the syn face of **2**). A reviewer has suggested, and we agree, that the much higher temperature required for the **2**−**1a** conversion admits the possibility that some other step (e.g. dissociation/reassociation of a −PPh$_2$ group or Cl$^-$) may mediate the net reaction, the mechanism of which is under investigation.