Stereomutation at an Octahedral Transition-Metal Center: Energetics of Hydride Transit between Syn and Anti Faces of the Bis(diphenylphosphinopropyl)(methyl)silyl (biPSi) Complex RuH(biPSi)(CO)$_2$

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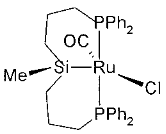
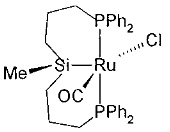
Summary: Reaction of $SiH(Me)(CH_2CH_2CH_2PPh_2)_2$, *"biPSiH", with* $Ru(PPh_3)_2(CO)_3$ *affords quantitatively the phosphinoalkylsilyl complex* RuH(biPSi)(CO)$_2$, *as a mixture of the crystallographically characterized syn diastereomer* ***3-s*** *and its anti correspondent* ***3-a****; subsequent treatment with* CCl_4 *then* $LiAl^2H_4$ *provides access to the deuterioisotopomer* Ru^{2}H(biPSi)(CO)$_2$, ***3-d****$_1$. Slow stereomutation of pure* ***3-s*** *to an equilibrium mixture* ***3-s/3-a*** *(4.5:1, 295 K) occurs with* $\Delta G^{\ddagger}_{295}$, *102(5) kJ* mol^{-1}; $\Delta H^{\ddagger}_{295}$, *113(7) kJ* mol^{-1}; $\Delta S^{\ddagger}_{295}$, *37(2) J* K^{-1} mol^{-1}; *this is not accompanied by incorporation of external* ^{13}CO, *shows only a minor isotope effect vs* ***3-d****$_1$, and is concluded to be nondissociative.*

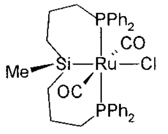
Stereomutation at an octahedral metal center is almost invariably identified with a dissociative pathway (I_D mechanism) and is frequently mediated through an isolable five-coordinate intermediate.[1] We have recently reported[2] that the 16-electron Ru(II) monocarbonyl *syn*-Ru(biPSi)(CO)Cl [biPSiH = SiH(Me)(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$] may be isolated as a pure diastereomer, **1-s**, that adopts a severely distorted trigonal bipyramidal (dist TBP[2,3]) geometry in the crystal and is stereochemically rigid in solution. On decarbonylation of the corresponding octahedral dicarbonyl *trans*-Ru(biPSi)(CO)$_2$Cl (**2**) in refluxing toluene, however, the same complex is formed as a mixture with its anti counterpart, **1-a**. This establishes a sequence (**1-s**−**2**−**1-a**) that is intriguing in the sense that interconversion between two five-coordinate structures is effectively mediated[2] *associatively* by a coordinatively saturated intermediate. The hydride counterpart RuH(biPSi)(CO)$_2$ of **2** was crystallographically characterized some time ago as[4] the syn diastereomer **3-s**, and we initially expected it to exhibit comparable behavior. This is not the case, however, as is described below. In fact on dissolution, pure **3-s** slowly attains equilibrium with its anti correspondent **3-a** by a mechanism that is nondissociative in CO; all attempts to observe a putative 16-e intermediate (***3-i***) to connect **3-s** with **3-a** (i.e., a five-coordinate hydridomonocarbonyl analogue of **1**) have so far failed; the dicarbonyl **3** is unchanged under all of the conditions that are routinely used to induce thermal, chemical, or photochemical decarbonylation; and treatment of the chloromonocarbonyl[2] **1** with hydride transfer reagents leads not to a hydride analogue, but rather to the detection in solution of a species concluded on the basis of its NMR properties to be a novel carbonyl monoanion, *cis*-[RuH$_2$(biPSi)(CO)]$^-$ (**4**, i.e., the H$^-$ adduct of ***3-i***).



1-s



1-a



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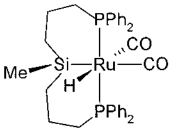
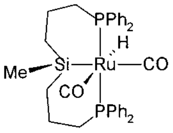
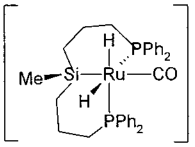


3-s



3-a



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The hydridodicarbonyl RuH(biPSi)(CO)$_2$ was originally isolated as yellow, X-ray quality crystals but in execrable yield (ca 7%)[4] from Ru$_3$(CO)$_{12}$ and shown to be a syn diastereomer (**3-s**), i.e., with the tridentate biPSi framework meridional and the Ru−*H* and Si−*Me* bonds on the same face of the molecule. We have since discovered that this complex is formed quantitatively during reflux over 17 h in toluene solution of the ligand precursor biPSiH with the mononuclear Ru(0) complex Ru(PPh$_3$)$_2$(CO)$_3$. Under these conditions, a mixture of two isomers is generated, of which the more abundant (NMR[4]) is **3-s**. NMR spectroscopy establishes that the minor constituent[5] also possesses a structure in which chelate P atoms are equivalent and H is trans to CO, identifying it as the anti correspondent **3-a** of **3-s**. These

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10.1021/om0100939 CCC: $20.00

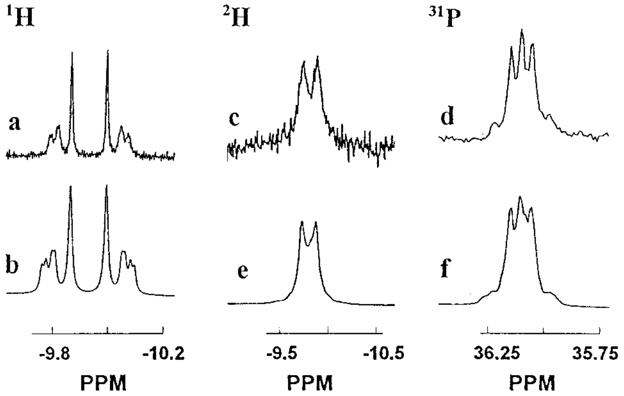

Figure 1. High-field (i.e., low-frequency) region of the ^{1}H NMR spectrum for anion **4**, generated under conditions described in the text: (a) observed; (b) simulated (using J values given in the text); and the ^{2}H and ^{31}P NMR spectra of the dideuterio analogue **4-*d*$_2$** (c, d) observed; (e, f) simulated.

stereochemical assignments are further supported by NOE difference measurements,[6] which confirm proximity between H and Me in **3-s** (i.e., consistent with its solid-state geometry) but not in **3-a**. The syn isomer **3-s** may be obtained free of its anti partner **3-a** by crystallization, or almost so by repeated washing of the initial product with ethanol then hexanes, but thereafter in solution slowly reverts to an equilibrium mixture **3-s**/**3-a** (4.5:1, 295 K; 3.6:1, 318 K).

Reflux (7 h) of the **3-s**/**3-a** mixture with a stoichiometric excess of CCl_4 in benzene solution yields the corresponding chloro complex Ru(biPSi)$(CO)_2$Cl (**2**), as a mixture[7] of two isomers (ca. 1.5:1), of which the major is that characterized[2] previously (i.e., trans). Further heating in toluene solution (24 h, 95 °C) affords the diastereomeric monocarbonyl analogue Ru(biPSi)(CO)-Cl (**1**), which rapidly takes up ^{m}CO (m = 12 or 13) to regenerate **2** or its isotopomer **2*** (i.e., with m = 13), as has been described.[2] As was anticipated, subsequent reactions with LiAl^{n}H$_4$ (n = 1 or 2; 20 °C, THF solution) resulted in replacement of chloride by hydride and could be adapted to regenerate **3** or to obtain each of three isotopomers (**3*** and the deuterated analogues **3-*d*$_1$**, **3*-*d*$_1$**). By contrast, treatment of **1** with LiAlH$_4$ yielded an extremely air-sensitive solution showing (reproducibly, NMR, THF-d_8) a single, odd-looking AB-like pattern centered at δ −9.94 in the ^{1}H NMR (high-field range: see Figure 1, a), which collapsed to a singlet on irradiation at the frequency of the single resonance (δ 36.0) observable in the ^{31}P NMR. Attempts to isolate any product led only to rapid decomposition, but on quenching with CO gas, **3** was formed cleanly and immediately in a composition significantly enriched (NMR) in the less stable anti diastereomer **3-a** vs the equilibrium ratio (ca. 2.4:1, cf. 4.5:1). Spectral simulations based on an AA′XX′ spin system (but not AX$_2$ or AXX′) adequately reproduce the appearance of the δ −9.94 resonance (Figure 1, a), using $J_{AA'}$ 4.7, $J_{XX'}$ 11.7, J_{AX} 68.1, $J_{AX'}$ −24.5, $J_{A'X}$ −27.0, $J_{A'X'}$ 66.8 Hz (see Figure 1, b), i.e., are consistent with a cis arrangement of pairs of hydrogen (A, A′) and phosphorus (X, X′) atoms that are coplanar (A, X and A′, X′ pairs trans to one another). Irradiation of the δ −9.94 signal in an NOE-difference experiment led to enhancement at the SiCH_3 and o-C$_6$H$_5$ hydrogen frequencies (i.e., at δ 0.11, 7.8, respectively), establishing proximity between Ru−H and Si−CH_3, i.e., a syn relationship of the latter. These data militate explicitly for an octahedral, anionic structure **4**, and accordingly repetition of the reaction sequence using LiAl^{2}H$_4$ led to observation of signals in ^{2}H and ^{31}P NMR spectra (see Figure 1, c and d) that could both be similarly simulated (see Figure 1, e and f) with $J_{AA'}$ −2.5, $J_{XX'}$ 11.4, J_{AX} 8.4, $J_{AX'}$ −1.9, $J_{A'X}$ −0.6, $J_{A'X'}$ 8.6 Hz, i.e., consistent with the isotopomer all-*cis*-[Ru^{2}H$_2$(biPSi)-(CO)]$^-$, **4-*d*$_2$**.

It is qualitatively obvious from the time required for **3-s**, **3-a** to equilibrate in solution (hours) that the diastereomers are separated by a substantial energy barrier (although they possess comparable thermodynamic stability: $K = 0.22$, 298 K; $\Delta G°_{298} \approx 5$ kJ mol^{-1}). Starting with material that is predominantly syn (**3-s**), the change in diastereomer ratio A$_{syn}$/A$_{anti}$ can be followed to equilibrium by using ^{1}H NMR (integrated intensity of Ru−H or Si−CH_3 signals at t_t, from t_0 to t_∞). Data so obtained followed rigorously first-order kinetics behavior, with k_1(syn:anti) 5.25×10^{-6}, 3.58×10^{-5}, and 1.72×10^{-4} s^{-1} at 295, 307, and 318 K, respectively, yielding an excellent straight line fit of ln-(k/T) vs T^{-1} (Eyring plot) and the following activation parameters: $\Delta G^{\ddagger}_{295}$, 102(5) kJ mol^{-1}; $\Delta H^{\ddagger}_{295}$, 113(7) kJ mol^{-1}; $\Delta S^{\ddagger}_{295}$, 37(2) J K^{-1} mol^{-1}. Measured rates were concentration independent and varied <20% in THF vs toluene. At 295 K, $k_1 = 4.36 \times 10^{-6}$ s^{-1} for stereomutation of the monodeuterio isotopomer **3-*d*$_1$** (i.e., corresponding to $k_{RuH}/k_{RuD} = 1.20$). Significantly, incorporation of external ^{13}CO (1 atm, 99 atom %, benzene solution, 295 K) into **3-s**/**3-a** was found to be much slower than the interconversion between the latter, so that during appropriate experiments only a trace of label, i.e., through formation of RuH(biPSi)(CO)(^{13}CO) (**3***), accumulated (NMR) over 24 h.

The kinetics data establish that the syn:anti stereomutation **3-s**:**3-a** is intramolecular. By contrast with the rapid, stereoselective label incorporation into **2**,[2] the rate of exchange with external ^{13}CO is negligible compared with k_1, effectively ruling out CO dissociation under the[8-10] strong trans influence of the biPSi silyl group as the pathway to an unsaturated intermediate. In

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(5) Minor isomer (**3-a**): ^{1}H NMR (C$_6$D$_6$) δ 0.52 (SiCH_3), −6.73 (t, RuH, $^2J_{PH}$ 22.0), (THF-d_8) δ 0.08 (SiCH_3), −7.06 (t, RuH); ^{13}C NMR (C$_6$D$_6$) δ 7.5 (SiCH$_3$), 20.5 (SiCH$_2$, SiCH$_2$$CH_2$), 32.4 (t, P$CH_2$), 199.0 (t, Ru$C$O, $^2J_{PC}$ 11.6), 203.9 (t, RuCO, $^2J_{PC}$ 7.8); ^{29}Si NMR (C$_6$D$_6$) δ −1.1 (t, $^2J_{SiP}$ 11.2); ^{31}P NMR (C$_6$D$_6$) δ 32.9. The Ph hydrogens were observed as complex multiplets in the δ 7.0−8.0 range; the methylene hydrogens for **3-a** were obscured by those due to **3-s**.

(6) Irradiation of the ^{1}H NMR signals of **3-s** at δ 0.38 or −6.30 each caused significant intensity enhancement of the other, while no similar effect was observed on irradiating those of **3-a** at δ 0.52 or −6.73. The irradiation at δ −6.30 or −6.73 also led to intensity enhancement at δ 8.10 or 7.95, respectively, and accordingly the corresponding ^{1}H NMR signals are assigned to Ph ortho hydrogens in **3-s** and **3-a**.

(7) Minor isomer: IR (KBr disk, cm^{-1}) 1964s, 2012w (ν_{CO}); ^{1}H NMR (C$_6$D$_6$) δ 0.36 (SiCH_3); ^{13}C NMR (C$_6$D$_6$) δ 4.0 (SiCH$_3$), 17.0 (SiCH$_2$), 21.2 (SiCH$_2$$CH_2$), 27.8 (t, P$CH_2$), 191.6 (t, Ru$C$O, $^2J_{PC}$ 10.4), 201.7 (t, RuCO, $^2J_{PC}$ 11.5); ^{29}Si NMR (C$_6$D$_6$) δ 1.7 (t, $^2J_{SiP}$ 16.0); ^{31}P NMR (C$_6$D$_6$) δ 13.9. The FAB MS for both **1** and **2** (mixtures of isomers) showed as the fragment at highest m/z (centered on 627 amu) a polyisotopic pattern attributable to Ru(biPSi)(CO)$^+$.

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further support of a profile that channels through a ruthenium dicarbonyl species, CO:^{13}CO "scrambling" in **3*** is observable at a rate that is qualitatively very similar to k_1. In a geometry where the sites trans to the labilizing Si and H centers are both occupied by unidentate CO, we see no justification for invoking preferential dissociation/reattachment[11] of a chelate phosphorus (i.e., biPSi) atom at Ru. Rapid incorporation of external CO would also be expected into any transient four-coordinate[9] Ru(0) species formed by reductive elimination (i.e., of Si−H); moreover substitution of Ru−H in **1-s** by Ru−D modifies k_1 in a way that is typical for a "normal secondary hydrogen isotope effect", thereby suggesting[12] a process that may involve a reduction in coordination number at Ru but ruling against Ru−H bond scission.[13]

On the basis of these observations, we propose that the diastereoisomerization **3-s**:**3-a** occurs *nondissociatively*, which requires either (i) concerted exchange of H and CO or (ii) twisting of the Ru−H bond around the Ru−Si axis, each of which might be expected to induce concomitant exchange of the two CO groups, as is observed (i.e., for **3***). Li and Hall have recently[14] concluded on the basis of a density functional theory analysis (B3LYP) that of possible mechanisms for cis to trans isomerization of the "pincer" dihydride[15] $IrH_2(CO)[C_6H_3(CH_2P^iPr_2)_2]$, a nondissociative trigonal twist is feasible at much lower energy than any dissociative mechanism. The calculated activation barrier of 24.0 kcal mol^{-1} to complete the required rearrangement, by two successive rotations of sets of atoms defining trigonal faces, is remarkably close (i.e., at ~100 kJ mol^{-1}) to the energetics reported here for the **3-s**:**3-a** interconversion, which would be effected by related consecutive rotations, so accomplishing i above. With regard to ii, although we searched carefully for direct evidence (e.g., $^1J_{Si-H}$ or $^2J_{P-Si}$)[16] for a three-center Si−H−Ru interaction in **3**, none was found, and a kinetic isotope effect (KIE) of 1.2 would appear to rule out Si−H bond reductive elimination/readdition.[17] In this last context it should be noted, however, that weak KIEs ($k_H/k_D = 1-2$) have been observed[18] for dissociative addition of dihydrogen to unsaturated transition-metal centers, as well as for site exchange in the rhodium cation $Rh(H)(^nH)[P(CH_2CH_2PPh_2)_3]^+$ ($n = 1$ or 2), where indeed the magnitude of the KIE ($k_H/k_D = 1.3$) has been taken to imply[19] some degree of H−H bonding during the intramolecular reorganization.

Anionic complexes resembling **4** have remained exceedingly rare since the investigation by Pez and Halpern of the catalytically active, *o*-metalated analogue[20] $[RuH_2(C_6H_4PPh_2)(PPh_3)_2]^-$ (K^+ salt). In fact the existence of **4** attests to a radical difference in Lewis acidity between the two 16-e congeners RuX(biPSi)(CO), X = Cl (i.e., **1**, which[2] has been isolated) or H (i.e., ***3-i***, which has not), reinforcing the arguments of Caulton et al.[21] concerning the relative stability of members of the isoelectronic family $RuH(X)(CO)(P^tBu_2Me)_2$ (**5**) that ranges through an extensive series of donors X including (as its weakest member[21]) hydride ion. Complexation of (putative) ***3-i*** with the latter, in preference to adopting a neutral, unsaturated state like that[22] of the silyl analogue $RuH(SiHPh_2)(CO)(P^tBu_2Me)_2$ (i.e., **5**, X = $-SiHPh_2$), further highlights the scarcity of five-coordinate Ru(II) centers from which π-donor ligands are absent.[23]

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(17) Which in order to interconvert **3-s**:**3-a** would also be required to mediate a crossover between the diastereomeric reaction manifolds that lead respectively to **3-s** and **3-a**, rather than following the microscopic reverse of the elimination step, which would simply regenerate the original stereochemistry (i.e., **3-s**).

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