

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

Xiaobing (“Joe”) Zhou and Stephen R. Stobart*

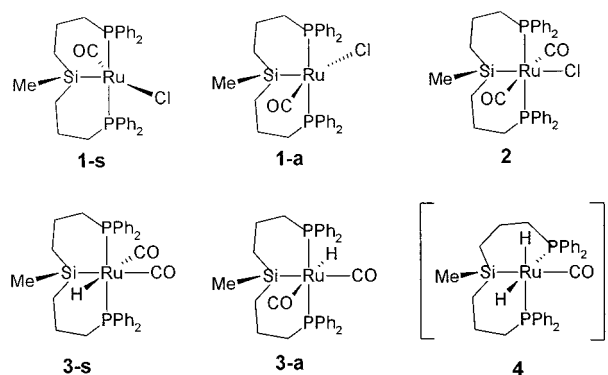
Department of Chemistry, University of Victoria, British Columbia, Canada V8W 2Y2

Received February 7, 2001

Summary: Reaction of $\text{SiH}(\text{Me})(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2$, “biPSiH”, with $\text{Ru}(\text{PPh}_3)_2(\text{CO})_3$ affords quantitatively the phosphinoalkylsilyl complex $\text{RuH}(\text{biPSi})(\text{CO})_2$, 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 $\text{Ru}^2\text{H}(\text{biPSi})(\text{CO})_2$, **3-d**. 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 ¹³CO, shows only a minor isotope effect vs **3-d**, 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 reported² that the 16-electron Ru(II) monocarbonyl syn- $\text{Ru}(\text{biPSi})(\text{CO})\text{Cl}$ [biPSiH = $\text{SiH}(\text{Me})(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2$] 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*- $\text{Ru}(\text{biPSi})(\text{CO})_2\text{Cl}$ (**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 mediated² associatively by a coordinatively saturated intermediate. The hydride counterpart $\text{RuH}(\text{biPSi})(\text{CO})_2$ of **2** was crystallographically characterized some time ago as⁴ 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 chloromonocarbonyl² **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*- $[\text{RuH}_2(\text{biPSi})(\text{CO})]^-$ (**4**, i.e., the H⁻ adduct of **3-i**).



The hydridodicarbonyl $\text{RuH}(\text{biPSi})(\text{CO})_2$ was originally isolated as yellow, X-ray quality crystals but in execrable yield (ca 7%)⁴ from $\text{Ru}_3(\text{CO})_{12}$ 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 $\text{Ru}(\text{PPh}_3)_2(\text{CO})_3$. Under these conditions, a mixture of two isomers is generated, of which the more abundant (NMR⁴) is **3-s**. NMR spectroscopy establishes that the minor constituent⁵ 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

(1) Blake, D. M.; Kubota, M. *J. Am. Chem. Soc.* **1970**, 92, 2578. Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, 97, 3380. Dombek, B. D.; Angelici, R. J. *J. Am. Chem. Soc.* **1976**, 98, 4110. Bray, J. M.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1987**, 2989. Vac, R.; Nelson, J. H.; Milosavljevic, E. B.; Solujic, L.; Fischer, J. *Inorg. Chem.* **1989**, 28, 4132. See also: Miller, J. S.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, 97, 1067. Johnson, B. F. G.; Rodger, A. *Inorg. Chem.* **1989**, 28, 1003.

(2) Bushnell, G. W.; Casado, M. A.; Stobart, S. R. *Organometallics* **2001**, 20, 601.

(3) Riehl, R.-F.; Jean, Y.; Eisenstein, O.; Pélissier, M. *Organometallics* **1992**, 11, 729. Albinati, A.; Bakmutov, 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.; Yymetis, A. B. *J. Am. Chem. Soc.* **1993**, 115, 7300. Auburn, M. J.; Holmes-Smith, R. D.; Stobart, S. R.; Bakshi, P. K.; Cameron, T. S. *Organometallics* **1996**, 15, 3032. Ujaque, G.; Maseras, F.; Eisenstein, O.; Liable-Sands, L.; Rheingold, A.; Yao, W.; Crabtree, R. H. *New J. Chem.* **1998**, 1493.

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

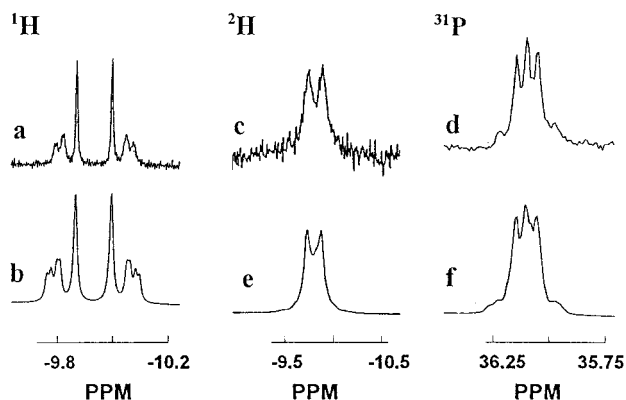


Figure 1. High-field (i.e., low-frequency) region of the ^1H NMR spectrum for anion **4**, generated under conditions described in the text: (a) observed; (b) simulated (using J values given in the text); and the ^2H and ^{31}P NMR spectra of the dideuterio analogue **4-d₂** (c, d) observed; (e, f) simulated.

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 $\text{Ru}(\text{biPSi})(\text{CO})_2\text{Cl}$ (**2**), as a mixture⁷ of two isomers (ca. 1.5:1), of which the major is that characterized² previously (i.e., trans). Further heating in toluene solution (24 h, 95 °C) affords the diastereomeric monocarbonyl analogue $\text{Ru}(\text{biPSi})(\text{CO})\text{Cl}$ (**1**), which rapidly takes up $m\text{CO}$ ($m = 12$ 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^nH_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-d₁**, **3*-d₁**). 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 $\delta -9.94$ in the ^1H 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 AX₂ or AXX') adequately reproduce the appearance of the $\delta -9.94$ resonance (Figure 1, a), using $J_{\text{AA}'} 4.7$, $J_{\text{XX}'} 11.7$, $J_{\text{AX}} 68.1$, $J_{\text{AX}'} -24.5$, $J_{\text{A'X}} -27.0$, $J_{\text{A'X}'} 66.8$ 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 $\delta -9.94$ signal in an NOE-difference experiment led to enhancement at the SiCH_3 and $o\text{-C}_6\text{H}_5$ hydrogen frequencies (i.e., at $\delta 0.11$, 7.8, respectively), establishing proximity between Ru-H and Si-CH₃, 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^2H_4 led to observation of signals in ^2H and ^{31}P NMR spectra (see Figure 1, c and d) that could both be similarly simulated (see Figure 1, e and f) with $J_{\text{AA}'} -2.5$, $J_{\text{XX}'} 11.4$, $J_{\text{AX}} 8.4$, $J_{\text{AX}'} -1.9$, $J_{\text{A'X}} -0.6$, $J_{\text{A'X}'} 8.6$ Hz, i.e., consistent with the isotopomer all-cis-[$\text{Ru}^2\text{H}_2(\text{biPSi})(\text{CO})$]⁻, **4-d₂**.

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; $\Delta G^\circ_{298} \approx 5$ kJ mol⁻¹). Starting with material that is predominantly syn (**3-s**), the change in diastereomer ratio $A_{\text{syn}}/A_{\text{anti}}$ can be followed to equilibrium by using ^1H NMR (integrated intensity of Ru-H or Si-CH₃ signals at t_i , from t_0 to t_∞). Data so obtained followed rigorously first-order kinetics behavior, with $k_1(\text{syn:anti})$ 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-d₁** (i.e., corresponding to $k_{\text{RuH}}/k_{\text{RuD}} = 1.20$). Significantly, incorporation of external ^{13}C (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 $\text{RuH}(\text{biPSi})(\text{CO})(^{13}\text{CO})$ (**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}C is negligible compared with k_1 , effectively ruling out CO dissociation under the⁸⁻¹⁰ strong trans influence of the biPSi silyl group as the pathway to an unsaturated intermediate. In

(5) Minor isomer (**3-a**): ^1H NMR (C_6D_6) δ 0.52 (SiCH_3), -6.73 (t, RuH , $^2J_{\text{PH}}$ 22.0), (THF- d_8) δ 0.08 (SiCH_3), -7.06 (t, RuH); ^{13}C NMR (C_6D_6) δ 7.5 (SiCH_3), 20.5 (SiCH_2 , SiCH_2CH_2), 32.4 (t, PCH_2), 199.0 (t, RuCO , $^2J_{\text{PC}}$ 11.6), 203.9 (t, RuCO , $^2J_{\text{PC}}$ 7.8); ^{29}Si NMR (C_6D_6) δ -1.1 (t, $^2J_{\text{SiP}}$ 11.2); ^{31}P NMR (C_6D_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 ^1H 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 $\delta -6.30$ or -6.73 also led to intensity enhancement at δ 8.10 or 7.95, respectively, and accordingly the corresponding ^1H 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}); ^1H NMR (C_6D_6) δ 0.36 (SiCH_3); ^{13}C NMR (C_6D_6) δ 4.0 (SiCH_3), 17.0 (SiCH_2), 21.2 (SiCH_2CH_2), 27.8 (t, PCH_2), 191.6 (t, RuCO , $^2J_{\text{PC}}$ 10.4), 201.7 (t, RuCO , $^2J_{\text{PC}}$ 11.5); ^{29}Si NMR (C_6D_6) δ 1.7 (t, $^2J_{\text{SiP}}$ 16.0); ^{31}P NMR (C_6D_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 $\text{Ru}(\text{biPSi})(\text{CO})^+$.

(8) Auburn, M. J.; Stobart, S. R. *Inorg. Chem.* **1985**, *24*, 318. Gambaro, J. J.; Hohman, W. H.; Meek, D. W. *Inorg. Chem.* **1989**, *28*, 4154. Kapoor, P.; Lövgqvist, K.; Oskarsson, Å. *Acta Crystallogr.* **1995**, *C51*, 611. Aizenberg, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 6456.

(9) Huang, D.; Streib, W. E.; Bollinger, J. C.; Caulton, K. G.; Winter, R. F.; Scheiring, T. *J. Am. Chem. Soc.* **1999**, *121*, 8087.

further support of a profile that channels through a ruthenium dicarbonyl species, $\text{CO}:\text{CO}^{13}\text{CO}$ "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 undentate CO, we see no justification for invoking preferential dissociation/reattachment¹¹ of a chelate phosphorus (i.e., biPSi) atom at Ru. Rapid incorporation of external CO would also be expected into any transient four-coordinate⁹ 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 suggesting¹² 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 recently¹⁴ concluded on the basis of a density functional theory analysis (B3LYP) that of possible mechanisms for cis to trans isomerization of the "pincer" dihydride¹⁵ $\text{IrH}_2\text{-(CO)[C}_6\text{H}_3(\text{CH}_2\text{P}^i\text{Pr}_2)_2]$, 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., $^1J_{\text{Si-H}}$ or $^2J_{\text{P-Si}}$)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 ($k_{\text{H}}/k_{\text{D}} = 1\text{--}2$) have been observed¹⁸ for dissociative addition of dihydrogen to unsaturated transition-metal centers, as well as for site exchange in the rhodium cation $\text{Rh}(\text{H})(\text{H})[\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3]^+$ ($n = 1$ or 2), where indeed the magnitude of the KIE ($k_{\text{H}}/k_{\text{D}} = 1.3$) has been taken to imply¹⁹ 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 analogue²⁰ $[\text{RuH}_2(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2]^-$ (K^+ salt). In fact the existence of **4** attests to a radical difference in Lewis acidity between the two 16-e congeners $\text{RuX}(\text{biPSi})(\text{CO})$, $\text{X} = \text{Cl}$ (i.e., **1**, which² 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 $\text{RuH}(\text{X})(\text{CO})(\text{P}^i\text{Bu}_2\text{Me})_2$ (**5**) that ranges through an extensive series of donors X including (as its weakest member²¹) hydride ion. Complexation of (putative) **3-i** with the latter, in preference to adopting a neutral, unsaturated state like that²² of the silyl analogue $\text{RuH}(\text{SiHPh}_2)(\text{CO})(\text{P}^i\text{Bu}_2\text{Me})_2$ (i.e., **5**, $\text{X} = \text{SiHPh}_2$), further highlights the scarcity of five-coordinate Ru(II) centers from which π -donor ligands are absent.²³

Acknowledgment. This research was supported by funding from the NSERC, Canada.

OM0100939

(10) Gusev, D. G.; Nadasdi, T. T.; Caulton, K. G. *Inorg. Chem.* **1996**, 35, 6772.

(11) El-Amouri, H.; Bahsoun, A. A.; Osborn, J. A. *Polyhedron* **1988**, 7, 2035. Rauscher, D. J.; Thaler, E. G.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1991**, 10, 2209. Kiss, G.; Horvath, I. T. *Organometallics* **1991**, 10, 3798.

(12) See: Carroll, F. A. *Perspectives on Structure and Mechanism in Organic Chemistry*; Brooks/Cole Publishing Co.: Pacific Grove, CA 93950, 1998; p 361, and references therein. For a further discussion see also: Hostetler, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, 114, 7629, and references therein.

(13) In this respect also being inconsistent with H transfer to a cis CO group, i.e., mediation through a transient five-coordinate Ru^{II} formyl.

(14) Li, S.; Hall, M. B. *Organometallics* **1999**, 18, 5682.

(15) Rytchinski, B.; Ben-David, Y.; Milstein, D. *Organometallics* **1997**, 16, 3786.

(16) Johnson, T. J.; Coan, P. S.; Caulton, K. G. *Inorg. Chem.* **1993**, 32, 4594. Lemke, F. R. *J. Am. Chem. Soc.* **1994**, 116, 11183. Delpech, F.; Sabo-Etienne, S.; Daran, J.-C.; Chaudret, B.; Hussein, K.; Marsden, C. J.; Barthelat, J.-C. *J. Am. Chem. Soc.* **1999**, 121, 6668.

(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**).

(18) Zhou, P.; Vitale, A. A.; San Filippo, J.; Saunders, W. H. *J. Am. Chem. Soc.* **1985**, 107, 8049.

(19) Heinekey, D. M.; van Roon, M. *J. Am. Chem. Soc.* **1996**, 118, 12134.

(20) Pez, G. P.; Grey, R. A.; Corsi, J. *J. Am. Chem. Soc.* **1981**, 103, 7528. Wilczynski, R.; Fordyce, W. A.; Halpern, J. *J. Am. Chem. Soc.* **1983**, 105, 2066.

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

(22) Heyn, R. H.; Huffman, J. C.; Caulton, K. G. *New J. Chem.* **1993**, 17, 797.

(23) Poulton, J. T.; Folting, K.; Strieb, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, 31, 3190. Poulton, J. T.; Sigalas, M. P.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1993**, 32, 5490. Caulton, K. G. *New J. Chem.* **1994**, 18, 25. Heyn, R. H.; Macgregor, S. A.; Nadasdi, T. T.; Ogasawara, M.; Eisenstein, O.; Caulton, K. G. *Inorg. Chim. Acta* **1997**, 259, 5.