This situation has to be contrasted to the result obtained during the reaction of phosphinoalkynes with $HRu_3(CO)_9(\mu\text{-}PPh_2)$, which shows that in this case hydride migration has occurred onto the C_α carbon, generating a primary alkyne subsequent to phosphorus bond breaking.[2]

The second product of the reaction, **3**, is an orange solid that presents very different spectroscopic properties compared to those of **2**. More specifically, the ^{31}P NMR spectrum shows a resonance at 57.5 ppm while a CH group is observed in the proton NMR spectrum at 3.64 ppm with a small coupling of 0.3 Hz with phosphorus. Moreover, the ^{13}C NMR spectrum confirms the presence of a CH group as a double doublet centered at 34.9 ppm (J_{CH} = 161.8 Hz, J_{PC} = 37 Hz), and, except for CO, Ph, and CMe_3 resonances, two signals are observed at 90.4 and 230.5 ppm.

The nature of **3** has been established by X-ray structure determination,[7] and the structure of the anionic part of **3** is shown in Figure 2. **3** is a dinuclear complex containing two $Fe(CO)_3$ units at bonding distances. This dinuclear unit is bridged by a five-electron organic ligand resulting from hydride migration onto the α–carbon of the alkynyl group and coupling of the β-carbon with carbon monoxide. This ligand is π-bonded to Fe(1) through phosphorus and through the carbon of the ketonic group and π-bonded to Fe(2) through the C(8)–C(9) double bond.

We may attribute the ^{13}C NMR resonances observed at 90.4 and 230.5 ppm to C(9) and C(7), respectively. Thus, the formation of **3** implies cluster fragmentation into a dinuclear species, migration of the hydride ligand onto the α-carbon of the alkynyl group, and insertion of a CO group between the β-carbon and Fe(1). The latter reaction has been precedented during acetylene–acetylide coupling via reactions of $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}C{\equiv}CR)$ complexes with alkynes.[8]

To conclude, the reaction of $Ph_2PC{\equiv}CCMe_3$ with $[PPh_4][HFe_3(CO)_{11}]$ in boiling ethyl acetate has led to the formation of two products. The main product, **2**, results from the cleavage of the phosphorus–alkynyl bond and subsequent migration of the hydride ligand onto the β-carbon, generating PPh_2 and $C{=}CH(CMe_3)$ bridging ligands. In the second product, **3**, cluster fragmentation into a dinuclear complex bridged by the $Ph_2PC(H){=}C(CMe_3)C(O)$ ligand is observed. This result illustrates further the great versatility of (diphenylphosphino)alkynes toward cluster complexes.

Acknowledgment. J.S. thanks the CICYT for a grant (No. PB86-0274).

Supplementary Material Available: Tables of final atomic coordinates, final anisotropic thermal parameters, and bond lengths and angles for $[PPh_4][Fe_3(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH(CMe_3))]$ and for $[PPh_4][Fe_2(CO)_6(\mu\text{-}Ph_2PCH{=}C(CMe_3)C(O))]$ (12 pages); listings of structure factor amplitudes (40 pages). Ordering information is given on any current masthead page.

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(7) Crystal data for $C_{49}H_{40}O_7P_2Fe_2{\cdot}CH_2Cl_2$; M_r 999.4; triclinic; a = 15.096 (2) Å, b = 16.332 (2) Å, c = 9.683 (1) Å, α = 92.60 (1)°, β = 95.21 (1)°, γ = 78.64 (1)°, V = 2330.0 (8) $Å^3$ (obtained as for ref 6); space group $P\bar{1}$; Z = 2; D_{calcd} = 1.424 $g{\cdot}cm^{-3}$; orange plate crystal (0.50 × 0.50 × 0.075 mm) sealed on a glass fiber; $\mu(Mo\ K\alpha)$ = 8.5 cm^{-1}; T = 293 K. **Data collection and processing**: intensity data were recorded by the $\theta/2\theta$ scan technique (scan width = 0.95° + 0.35° tan θ; scan speed = 1.0–6.9 $deg{\cdot}min^{-1}$). A set of 5827 independent reflections was collected ($1.5 < \theta < 22.5°$; $\pm h,\pm k,l$) and corrected for Lorentz and polarization effects (see ref 6). Standard intensity reflections, recorded every 2 h, showed no significant fluctuations. Empirical absorptions corrections (North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 351–359) were applied: T_{min} = 0.82; T_{max} = 1.00. A total of 4186 reflections with $I > 3\sigma(I)$ were used in structure solution and refinement. **Structure determination**: Structure was solved and refined as in ref 6. All non-hydrogen atoms were refined anisotropically but phenyl rings which were refined as isotropic rigid groups (C–C = 1.395 Å). Hydrogen atoms were located on a difference Fourier map at their expected positions and introduced in calculations in constrained geometry (C–H = 0.97 Å) except that bonded to C(8), which was allowed to vary. Scattering factors were those of ref 6. The final full-matrix least-squares refinement converged to R = 0.032 and R_w = 0.032 with unit weights. S had the value 1.1 with 4186 observations and 319 variables. A final difference Fourier map showed a residual electron density of 0.3 $e/Å^3$.

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Reaction between Transition-Metal Nucleophiles and Alkanedioyl Dichlorides: Preparation of Five- and Six-Membered Metal-Substituted Lactone Complexes $(\eta^5\text{-}C_5H_5)(CO)_3M\text{–}\overline{C{:}CH(CH_2)_nC(O)O}$ (M = Mo, W; n = 1, 2)

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Summary: Unsaturated, unconjugated five- and six-membered transition-metal-substituted lactone complexes $(\eta^5\text{-}C_5H_5)(CO)_3M\text{–}\overline{C{:}CH(CH_2)_nC(O)O}$ (M = Mo, W; n = 1, 2) are prepared by reacting $Na[(\eta^5\text{-}C_5H_5)M(CO)_3]$ with succinyl and glutaryl dichlorides. The reaction mechanism involves the formation of a monometallic alkanedioyl chloride complex, followed by a base-assisted cyclization reaction.

The reaction of transition-metal nucleophiles with α,ω-dihaloalkanes is known to produce dimetalloalkanes,[1] monosubstituted alkyl halides,[2] or oxacycloalkylidenes,[3] depending on the metals and halides involved. In contrast, the reaction between transition-metal nucleophiles and α,ω-alkanedioyl dihalides only produce dimetallic alkanedioyl complexes.[2,4] For example, King, Petit, and their co-workers prepared several $FpC(O)\text{–}(CH_2)_n\text{–}(O)CFp$ (Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$, n = 2–4) by reacting the strongly nucleophilic Fp^- with the corresponding alkanedioyl dichlorides, presumably via a disubstitution mechanism.[2,4a] We were attempting to prepare heterobimetallic bridging bis(acyl) complexes by successive acylations of bis(acyl) dichloride with two different metal anions. Herein we wish to describe some unexpected results we obtained from the reaction of $Na[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (M = Mo, **1a**; M = W, **1b**) with succinyl and glutaryl dichlorides. Instead of the expected bimetallic products, we isolated novel unsaturated and unconjugated five- and six-membered metal-substituted lactones $(\eta^5\text{-}C_5H_5)(CO)_3M\text{–}\overline{C{:}CH(CH_2)_nC(O)O}$ (M = Mo, n = 1, **2a**; M = W, n = 1, **2b**; M = Mo, n = 2, **3a**; M = W, n = 2, **3b**) under a variety of conditions.

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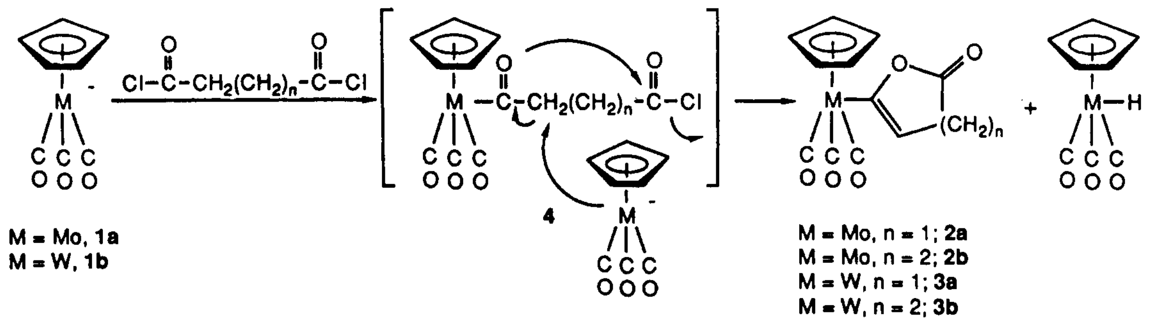
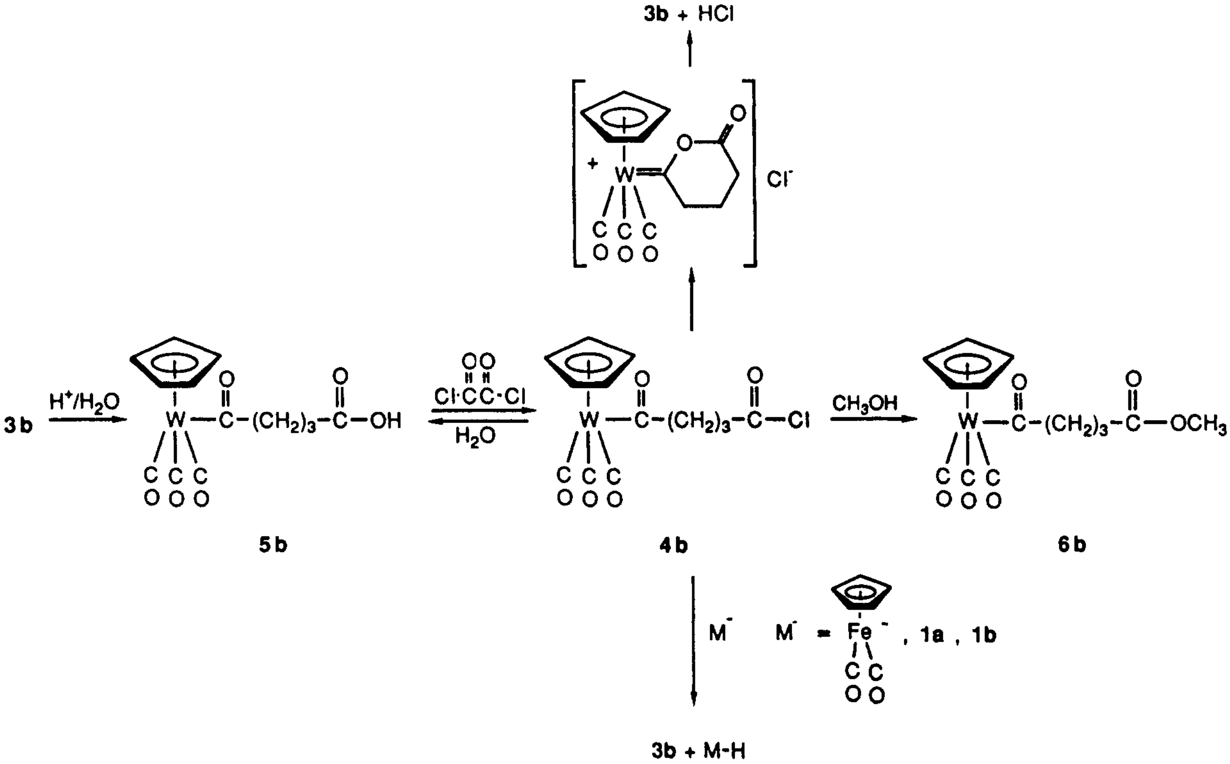
Scheme I



Scheme II



In a typical reaction, a solution of **1a** was prepared by refluxing 2.0 g (7.6 mmol) of $Mo(CO)_6$ with an equivalent amount of NaC_5H_5 in 75 mL of THF for 24 h. To this solution at room temperature was added 0.42 mL of succinyl chloride (3.8 mmol). The reaction mixture was stirred for 30 min, during which time the color of the solution changed from yellow to brown-orange. Solvent was removed under reduced pressure, and a waxy solid was obtained. A ^{1}H NMR spectrum of this solid in $CDCl_3$ showed the formation of **2a** and $H(\eta^5\text{-}C_5H_5)Mo(CO)_3$. Complex **2a** may be purified by dissolving the residue in CH_2Cl_2 and passing it through a silica gel column (20 × 2.5 cm). Initial elution removed the unreacted $Mo(CO)_6$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$, the latter formed by the decomposition of $H(\eta^5\text{-}C_5H_5)Mo(CO)_3$. This is followed by a slow elution of a yellow band of complex **2a** (0.72 g, 2.2 mmol 29% based on $Mo(CO)_6$). Complex **2b** may be prepared analogously (0.78 g, 1.8 mmol, 33%). Complexes **3a** and **3b** were also prepared following similar procedures by the reaction of **1a** and **1b** with glutaryl dichloride (**3a**, 35%; **3b**, 38%). Complexes **2** and **3** are isolated as yellow crystalline solids that are stable in air at ambient temperature for several hours without noticeable decomposition. In solution, however, they show high air-sensitivity. They are characterized by ^{1}H and ^{13}C NMR, IR, and elemental analysis.[5]

The reaction mechanism appears to involve the acyl substitution of only one chloride from the bis(acyl) dichloride. Instead of acylating the second acyl chloride, a second metal anion acts as a base to induce the cyclization of intermediate 4 into the observed products (Scheme I). There are several examples of metal anions displacing only

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(5) Compound **2a**: IR (KBr, ν_{CO}, cm^{-1}) 2030 (s), 1954 (s), 1920 (vs), 1778 (m), 1753 (m); ^{1}H NMR (200 MHz, $CDCl_3$, 23 °C) δ 5.64 (t, 1 H, J = 2.1 Hz, C:CH), 5.53 (s, 5 H, Cp), 3.10 (d, 2 H, J = 2.1 Hz, CH_2C(O)); ^{13}C NMR (50 MHz, $CDCl_3$, 23 °C) δ 236.6, 225.9 (M–CO), 180.1 (C(O)O), 164.8 (C:CH), 122.7 (C:CH), 93.0 (Cp), 35.0 (CH_2). Anal. Calcd for $C_{12}H_8O_5Mo$: C, 43.93; H, 2.44. Found: C, 43.69; H, 2.39. Compound **2b**: IR (KBr, ν_{CO}, cm^{-1}) 2034 (s), 1959 (s), 1926 (vs), 1774 (m), 1753 (m); ^{1}H NMR (200 MHz, $CDCl_3$, 23 °C) δ 5.68 (t, 1 H, J = 2.4 Hz, C:CH), 5.61 (s, 5 H, Cp), 3.15 (d, 2 H, J = 2.4 Hz, CH_2C(O)); ^{13}C NMR (50 MHz, $CDCl_3$, 23 °C) δ 225.9, 215.7 (M–CO), 179.0 (C(O)O), 169.2 (C:CH), 123.8 (C:CH), 91.6 (Cp), 35.3 (CH_2). Anal. Calcd for $C_{12}H_8O_5W$: C, 34.64; H, 1.94. Found: C, 34.33; H, 1.83. Compound **3a**: IR (KBr, ν_{CO}, cm^{-1}) 2025 (s), 1951 (s), 1930 (vs), 1738 (s); ^{1}H NMR (200 MHz, $CDCl_3$, 23 °C) δ 5.51 (t, 1 H, J = 4.6 Hz, C:CH), 5.49 (s, 5 H, Cp), 2.53 (t, 2 H, J = 6.4 Hz, CH_2C(O)), 2.35 (m, 2 H, CHCH_2CH$_2$); ^{13}C NMR (50 MHz, $CDCl_3$, 23 °C) δ 238.1, 227.1 (M–CO), 170.4 (C(O)O), 160.4 (C:CH), 124.4 (C:CH), 93.4 (Cp), 29.2, 22.2 (CH_2). Anal. Calcd for $C_{13}H_{10}O_5Mo$: C, 45.64; H, 2.75. Found: C, 45.29; H, 2.75. Compound **3b**: IR (KBr, ν_{CO}, cm^{-1}) 2017 (s), 1940 (s), 1916 (vs), 1733 (s); ^{1}H NMR (200 MHz, $CDCl_3$, 23 °C) δ 5.62 (t, 1 H, J = 4.6 Hz, C:CH), 5.58 (s, 5 H, Cp), 2.52 (t, 2 H, J = 7.2 Hz, CH_2C(O)), 2.29 (m, 2 H, CHCH_2CH$_2$); ^{13}C NMR (50 MHz, $CDCl_3$, 23 °C) δ 227.5, 217.7 (M–CO), 170.6 (C(O)O), 145.6 (C:CH), 125.9 (C:CH), 92.0 (Cp), 29.1, 22.3 (CH_2). Anal. Calcd for $C_{13}H_{10}O_5W$: C, 36.31; H, 2.34. Found: C, 36.40; H, 2.23.

one halide from dihaloalkanes.[2] However, to the best of our knowledge, this is the first example involving the selective replacement of a single halide by a metal anion from an aliphatic alkanedioyl dihalide.[6]

We investigated these reactions under various conditions in order to gain more insight into the mechanism. When a fivefold excess of **1** is used, **3** is formed in lower yields (5–7%). No bimetallic alkanedioyl complexes were observed. Attempts to isolate intermediate **4** by a slow addition of **1** into a THF solution containing excess alkanedioyl dichloride (up to 5 equiv) at −78 °C were unsuccessful. However, we were able to prepare **4b** by a two-step reaction sequence. Treatment of **3b** with aqueous HCl in THF afforded the corresponding carboxylic acid (**5b**),[7] which was then converted into acyl chloride **4b**[7] by treating with 1.2 equiv of oxalyl chloride at 35 °C for 20 min in CH_2Cl_2 (Scheme II). Complex **4b** may be trapped by H_2O and CH_3OH to form **5b** and $(\eta^5\text{-}C_5H_5)(CO)_3WC(O)(CH_2)_3C(O)OCH_3$ (**6b**),[7] respectively. It cannot be isolated, however, since upon solvent removal, it converts completely into **3b**. The removal of HCl in vacuo presumably drives the reaction toward **3b**. There are several examples of spontaneous cyclization of ω-bromoacyl derivatives into 2-oxacyclopentylidenes.[3] Since acyl chlorides are more reactive than alkyl bromides, our reaction may go through a similar cyclization sequence. This is followed by the deprotonation of the acidic proton α to the carbene carbon by a chloride ion to produce the observed products.[8,9]

Although a base is not required for the transformation from **4** to **3**, we believe the metal anion is important in assisting the cyclization reaction. A solution of **4b** prepared in situ decomposes slowly into $(\eta^5\text{-}C_5H_5)(CO)_3WCl$ with a half-life of approximately 2 h. With the addition of M^- ($M = (\eta^5\text{-}C_5H_5)Fe(CO)_2$, $(\eta^5\text{-}C_5H_5)Mo(CO)_3$, $(\eta^5\text{-}C_5H_5)W(CO)_3$), **3b** and the corresponding M–H are formed within a few minutes. Especially noteworthy is the reaction between **4b** and Fp^-. Our result indicates that the formation of lactone (elimination) is preferred over the acylation of the second acyl chloride (substitution) even with the powerful nucleophile Fp^-. This suggests that the known reaction between Fp^- and alkanedioyl dichlorides may go through a different route rather than the simple disubstitution mechanism. This possibility is currently under investigation.

Acknowledgment. We thank the Research Corp. and the donors of Petroleum Research Fund, administered by the American Chemical Society, for their financial support. Funds for the purchase of the IBM AF 200-MHz FT NMR spectrometer were provided by the National Science Foundation (RUI Grant Number CHE-8513187) and the Fletcher Jones Foundation.

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(6) One example of a tetracarbonylferrate(II) replacing one chloride from phthaloyl dichloride was reported: Mitsudo, T. A.; Watanabe, Y.; Tanaka, M.; Yamamoto, K.; Takegami, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 305.

(7) Compound **4b**: IR ($CDCl_3$, cm^{-1}) 2021 (s), 1921 (vs), 1780 (m), 1626 (m); ^1H NMR (200 MHz, $CDCl_3$, 23 °C) δ 5.59 (s, 5 H, Cp), 3.00 (t, 2 H, J = 6.8 Hz, $WC(O)CH_2$), 2.89 (t, 2 H, J = 7.3 Hz, $CH_2C(O)Cl$), 1.78 (m, 2 H, $CH_2\mathit{CH}_2CH_2$). Compound **5b**: IR (KBr, cm^{-1}) 2950–3110 (br, m), 2008 (s), 1903 (vs), 1718 (s), 1625 (s); ^1H NMR (200 MHz, $CDCl_3$, 23 °C) δ 5.57 (s, 5 H, Cp), 3.01 (t, 2 H, J = 6.9 Hz, $WC(O)CH_2$), 2.28 (t, 2 H, J = 7.4 Hz, $C\mathit{H}_2C(O)OH$), 1.72 (m, 2 H, $CH_2\mathit{CH}_2CH_2$); ^{13}C NMR (50 MHz, $CDCl_3$, 23 °C) δ 244.9 (W–C(O)), 226.0, 220.0 (W–CO), 178.6 (C(O)OH), 95.3 (Cp), 65.5, 32.8, 20.2 (CH_2). Anal. Calcd for $C_{13}H_{12}O_6W$: C, 34.85; H, 2.70. Found: C, 35.19; H, 2.65. Compound **6b**: IR ($CHCl_3$, cm^{-1}) 2018 (s), 1925 (vs), 1731 (m), 1626 (m); ^1H NMR (200 MHz, $CDCl_3$, 23 °C) δ 5.56 (s, 5 H, Cp), 3.63 (s, 3 H, OCH_3), 2.97 (t, 2 H, J = 7.0 Hz, $WC(O)CH_2$), 2.22 (t, 2 H, J = 7.4 Hz, $\mathit{CH}_2C(O)OCH_3$), 1.69 (m, 2 H, $CH_2\mathit{CH}_2CH_2$); ^{13}C NMR (50 MHz, $CDCl_3$, 23 °C) δ 244.3 (W–C(O)), 226.1, 220.0 (W–CO), 173.6 ($C(O)OCH_3$), 95.2 (Cp), 65.6 ($C_\alpha H_2$), 51.3 (OCH_3), 33.0, 20.4 ($\mathit{C}H_2$). This compound is identical with a sample prepared from $Na(\eta^5\text{-}C_5H_5)W(CO)_3$ and methyl 4-(chloroformyl)butyrate.

(8) The acidity of these protons are well-documented: Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1230.

(9) This cyclic carbene could also be an intermediate in the reaction between **4** and **1**, although we have no evidence for its formation. The reaction between a cationic molybdenum oxacyclopentylidene and $(\eta^5\text{-}C_5H_5)W(CO)_3^-$ was reported to form a bimetallic compound in good yield.[3c]

Chiral and C_2-Symmetrical Bis(oxazolinylpyridine)rhodium(III) Complexes: Effective Catalysts for Asymmetric Hydrosilylation of Ketones

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Received October 20, 1988

Summary: Chiral bis(oxazolinylpyridine)rhodium(III) trichloride complexes **2a–c** were synthesized by the reaction of rhodium(III) trichloride with bis(oxazolinylpyridine) (pybox: *py*ridine, *b*is(*ox*azolinyl)) derivatives **1a–c**, which are newly designed as chiral ligands and prepared from pyridine-2,6-dicarboxylic acid and (*S*)-valinol, (*S*)-*sec*-leucinol, and (*S*)-*tert*-leucinol, respectively. We have examined the asymmetric hydrosilylation of ketones with the rhodium complexes **2a–c** and diphenylsilane to find extremely high enantioselectivity in the formation of secondary alcohols having the *S* configuration.

Chiral catalysts in the reduction of ketones have been currently required to attain extremely high level of enantioselectivity.[1] However in the hydrosilylation of ketones any chiral phosphines could not achieve higher optical yields,[2] while it is noteworthy that some nitrogen-containing organic ligands reported by Brunner's group can attain excellent results, more than 90% ee.[3] In terms of molecular and enantioface recognition, we have been interested in designing chiral organic molecules as ligands for transition-metal catalysts. We report here new chiral and C_2-symmetrical terdentate pyridine ligands and their rhodium(III) complexes, which exhibit high enantioselectivity in the hydrosilylation of several ketones.

Our design of the pyridine ligands **1a–c**, *b*is(*ox*azolinyl*py*ridines) (pybox), is distinctive in that the two chiral oxazoline rings having the two bulky alkyl groups make a chiral and C_2-symmetrical concave. In the rhodium complexes **2a–c**, the two alkyl groups are placed as closely

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