$(p\text{-}CH_3C_6H_4NC)_8Rh_2I_2^{2+}$ (Rh–Rh, 2.785 (2); Rh–I, 2.735 (1) Å).[4] Despite the fractional oxidation state of rhodium (average value 5/3) an electron counting scheme which assigns a simple electron pair bond between each pair of rhodium atoms results in an 18-electron count for each of the metal centers.

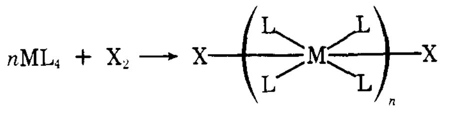
The solution behavior of these cations is complex. It is dominated by dissociation into smaller fragments by the following equations:[5]

$$(RNC)_{12}Rh_3X_2^{3+} \rightleftharpoons (RNC)_8Rh_2X_2^{2+} + (RNC)_4Rh^+ \quad (1)$$

$$(RNC)_8Rh_2X_2^{2+} \rightleftharpoons (RNC)_4RhX_2^+ + (RNC)_4Rh^+ \quad (2)$$

Dissociation has been monitored by both electronic and infrared spectral changes. The behavior of $[(n\text{-}C_4H_9NC)_{12}Rh_3I_2]I_2$ (**2**) is typical. Its electronic spectral changes are shown in Figure 2. The violet color due to the characteristic absorption at 525 nm fades in 2–4 h to give yellow (dichloromethane)[6] or yellow-brown (acetonitrile)[6] solutions containing an equilibrium mixture of $(n\text{-}C_4H_9NC)_8Rh_2I_2^{2+}$, $(n\text{-}C_4H_9NC)_4RhI_2^+$, and $(n\text{-}C_4H_9NC)_4Rh^+$. The spectra of the equilibrated solutions may be quantitatively reproduced by preparing solutions containing a 2:1 ratio of $[(n\text{-}C_4H_9NC)_4Rh][BPh_4]$ and $[(n\text{-}C_4H_9NC)_4RhI_2][BPh_4]$ at the appropriate concentrations. The dissociation reaction 1 is photoaccelerated; exposure of a 5×10^{-5} M solution of **2** to room light causes the violet color to bleach within 3 min. The infrared spectra of dichloromethane solutions of **2** initially show an isocyanide stretching frequency at 2218 cm^{-1}. As dissociation proceeds, bands at 2229 and 2182 cm^{-1} grow owing to the formation of $(n\text{-}C_4H_9NC)_8Rh_2I_2^{2+}$ and $(n\text{-}C_4H_9NC)_4Rh^+$, respectively. Subsequently a fourth band at 2248 cm^{-1} grows owing to the formation of $(n\text{-}C_4H_9NC)_4RhI_2^+$. These changes due to dissociation are reversible. Evaporation of dissociated solutions prepared from $[(RNC)_{12}Rh_3I_2]I_3$ yields violet crystals of the starting complex.

The dissociation of $(RNC)_{12}Rh_3I_2^{2+}$ may provide a model for the breakup of longer linear chain species such as the partially oxidized platinum cyanides and oxalates.[7,8] In this context it is also interesting to note that electron precise complexes may be generated by addition of a two-electron oxidant such as iodine or bromine across any number of planar d^8 complexes (ML_4) as represented by eq 3. For the rhodium isocyanide



(3)

system the products have n = 1, 2, or 3 with the composition controlled largely by the stoichiometry of the reactants. For this system the length of the chains which may be prepared is probably limited to n = 3 because of the increase in total charge that accompanies the incorporation of each $(RNC)_4Rh^+$ unit into the chain. For uncharged d^8 complexes with sterically undemanding ligands, however, it should be possible to obtain even longer chains.

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Supplementary Material Available: A table of atomic positions and thermal parameters (3 pages). Ordering information is given on any current masthead page.

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(6) In dichloromethane solution under these dilute conditions little $[(n\text{-}C_4H_9NC)_8Rh_2I_2]^{2+}$ (λ_{max} 448 nm) is present and the solution is yellow, whereas in acetonitrile an appreciable amount of $[(n\text{-}C_4H_9NC)_8Rh_2I_2]^{2+}$ is present and is responsible for the brown color.

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Virtually Complete Enantioface Differentiation in Carbonyl Group Reduction by a Complex Aluminum Hydride Reagent[1]

Sir:

Based on the pioneering efforts of Cram and co-workers, molecules containing an axially dissymmetric 1,1′-binaphthyl moiety were shown to have extremely high ability of chiral recognition.[2] Here we describe an effective asymmetric reduction of prochiral carbonyl compounds with a hydride reagent containing such chiral auxiliary ligand. In certain cases, the enantioselectivity is virtually complete.

We used complex aluminum hydride reagents of type **2** (empirical formula) prepared in situ from $LiAlH_4$, optically pure 2,2′-dihydroxy-1,1′-binaphthyl (**1**),[3] and a hydroxylic compound (R′OH). A typical experimental procedure is exemplified by the reduction of butyrophenone. To a 1.63 M THF solution of $LiAlH_4$ (8.31 mmol) placed under argon atmosphere was added ethanol in THF (2.00 M, 8.40 mmol) at 0 °C. Then (*S*)-(−)-**1** ($[\alpha]^{20}_D$ −38.0° (*c* 1.00, THF)) in THF (0.65 M, 8.43 mmol) was added at 0 °C[4] and the resulting white, cloudy mixture was stirred at room temperature for 1 h.[5] The chiral reagent thus formed was cooled to −100 °C and to this was added a 1.00 M THF solution of butyrophenone (2.50 mmol). The mixture was stirred at this temperature for 3 h and then at −78 °C for 16 h and quenched by adding 2 N HCl at −78 °C. Extractive workup with ether followed by evaporative distillation afforded optically pure (*S*)-(−)-phenylpropylcarbinol ((*S*)-**3** (R = $n\text{-}C_3H_7$), 291 mg, 78%

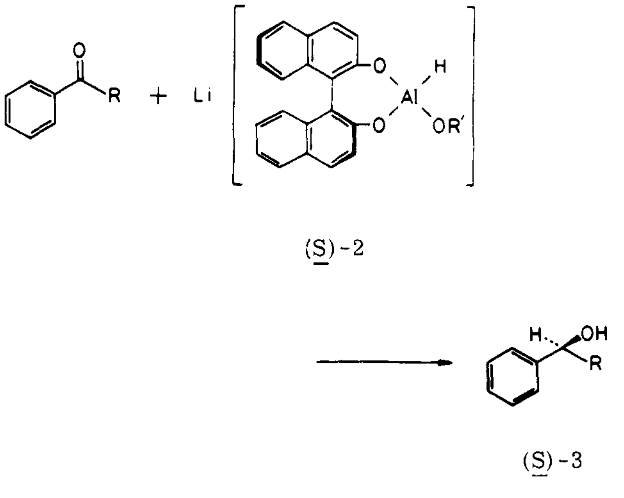

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Table I. Asymmetric Reduction of Carbonyl Compounds by **2** ($R'O = C_2H_5O$)[a]

entry	substrate	hydride reagent	carbinol product chemical yield, %[b]	$[\alpha]^{26}_D$, deg (*c*, solvent)	optical yield, % ee (confign)
1	C_6H_5CDO[c]	(*R*)-**2**	75	−1.3 (6.34, cyclopentane)	82[d,e] (*R*)
2	$C_6H_5COCH_3$	(*R*)-**2**	61	+0.415 (neat)[f]	95[g,h] (*R*)
3	$C_6H_5COCH_2CH_3$	(*S*)-**2**	62	−0.284 (neat)[f,i]	98[d,j] (*S*)
4	$C_6H_5COCH_2CH_2CH_3$	(*S*)-**2**	78[k]	−45.2 (4.81, benzene)[l]	100[g,m,n] (*S*)
5	$C_6H_5COCH_2CH_2CH_2CH_3$	(*S*)-**2**	64	−0.200 (neat)[f,l]	100[g,m,o] (S))
6	$C_6H_5COCH(CH_3)_2$	(*S*)-**2**	68	−0.172 (neat)[f]	71[d,p] (*S*)

[a] The reaction was carried out using ~3 equiv of **2** at −100 °C for 2–3 h and then at −78 °C for 16 h. [b] Determined by GLC. The remainder was unreacted carbonyl compound. [c] Reaction at −100 °C for 3 h. [d] Determined by comparison of the magnitude of optical rotation with the highest reported value. [e] $[\alpha]^{20}_D(\max)$ +1.58° (*c* 7.07, cyclopentane). See ref 10a. [f] α_D value ($l = 0.01$ dm). [g] The $[\alpha]_D$ or α_D value was compared with that of authentic sample obtained by optical resolution. [h] $[\alpha]^{21}_D(\max)$ −43.5° (neat): MacLeod, R.; Welch, F. J.; Mosher, H. S. *J. Am. Chem. Soc.* **1960,** *82*, 876. [i] Measured at 27 °C. [j] $[\alpha]^{27.2}_D$ +29.1° (neat). See reference in footnote *h*. [k] Isolated yield. [l] Measured at 22 °C. [m] NMR spectrum of the MTPA ester is consistent with this value. [n] $[\alpha]_D(\max)$ +43.6° (*c* 4.79, benzene) or −45.9° (*c* 5.15, benzene). See ref 7. [o] $\alpha^{20}_D(\max)$ +20° (neat, $l = 1$ dm): Horeau, A.; Guetté, J. P.; Weiolmann, R. *Bull. Soc. Chim. Fr.* **1966,** 3513. [p] $[\alpha]_D(\max)$ −24.6° (neat). See reference in footnote *h*.

Table II. Asymmetric Reduction of Acetophenone[a]

entry	hydride reagent (R′O)	reaction conditions, *T*, °C (time, h)	carbinol product $[\alpha]_D$, deg (*c*, *T* in °C)[b]	optical yield, % ee (confign)
1	(*R*)-**2** (CH_3O)	30 (5)	+42.9 (1.01, 23)	73 (*R*)
2	(*R*)-**2** (CH_3O)	−78 (5)	+51.6 (1.01, 23)	87 (*R*)
3	(*R*)-**2** (C_2H_5O)	30 (5)	+38.4 (1.00, 23)	64 (*R*)
4	(*R*)-**2** (C_2H_5O)	−20 (5)	+45.3 (1.01, 23)	77 (*R*)
5	(*R*)-**2** (C_2H_5O)	−50 (5)	+49.6 (1.02, 23)	84 (*R*)
6	(*R*)-**2** (C_2H_5O)	−78 (5)	+53.2 (1.00, 24)	90 (*R*)
7	(*R*)-**2** (i-C_3H_7O)	30 (5)	+27.4 (1.00, 24)	46 (*R*)
8	(*R*)-**2** (t-C_4H_9O)	30 (5)	+22.2 (1.00, 24)	38 (*R*)
9	(*R*)-**2** (CF_3CH_2O)	30 (5)	−8.2 (1.01, 24)	14 (*S*)[c]
10	(*R*)-**2** (C_6H_5O)	30 (5)	+9.9 (1.01, 23)	17 (*R*)
11	(*R*)-**2** (2,6-(t-$C_4H_9)_2C_6H_3O$)	30 (5)	−25.8 (1.02, 23)	44 (*S*)
12	(*R*)-**2** (AlO)[d]	30 (5)	+19.4 (0.99, 24)	33 (*R*)
13	(*R*)-**1** and AlH_3	30 (5)	+6.1 (1.01, 24)	10 (*R*)

[a] Reaction was performed using 2 equiv of the hydride reagent in THF. Chemical yield of the reaction at 30 °C was 95–100%, whereas the low-temperature reaction afforded the carbinol in ~60% yield. The remainder was unreacted acetophenone. [b] In cyclopentane. The specific rotation was significantly concentration dependent and this was determined using the standard calibration curve. [c] Reaction at −100 (2 h) and −78 °C (16 h) gave 42% ee. [d] Water (0.5 equiv) was used for the preparation of the hydride reagent.

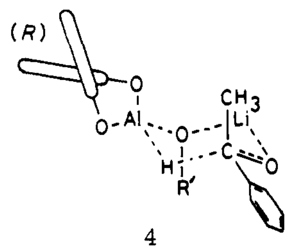
yield). Recrystallization of the residue from benzene gave back (−)-**1** in 70–90% yield as reusable form without any noticeable racemization.

Properties of a GLC-purified crystalline sample of this carbinol were compared directly with those of the authentic optically pure specimen which was prepared by careful optical resolution via the hydrogen phthalate brucine salt.[6] Melting point and mixture melting point were 46–47 °C. Both samples exhibited entirely the same magnitude of specific rotation, $[\alpha]^{22}_D$ −45.2° (*c* 4.81, benzene).[7] The optical purity of the carbinol was further substantiated by NMR analysis after converting to the ester of α-methoxy-α-trifluoromethylphenylacetic acid (MTPA).[8] The MTPA ester obtained from the optically pure carbinol and (*S*)-(−)-MTPA chloride ((*S*)-(−)-MTPA supplied from Aldrich, 99+%) gave a single methoxyl signal and a doubleting doublet due to the benzylic proton, whereas the diastereomeric esters formed from the racemic carbinol exhibited two sets of the signals with equal intensities.

Some other examples are given in Table I. Thus this complex aluminum hydride reagent gave exceptionally high optical yields in production of alkylphenylcarbinols as well as benzyl-α-*d* alcohol.[9-11] Since both (*R*)- and (*S*)-**1** are readily accessible in optically pure form,[3] this method allows the synthesis of both enantiomers of carbinols from carbonyl compounds. The reduction of simple dialkyl ketones did not give satisfactory optical yield.[12]

In connection with the detailed reaction mechanism, the following observations gained in the reaction of acetophenone would deserve some comment. (1) The observed enantioface differentiation is kinetically controlled by the relative stabilities of the diastereomeric transition states in the reaction of **2** and a carbonyl compound and is not a result of thermodynamic control governed by the stability of the resulting aluminum or lithium alkoxide product.[13] (2) As usual, the optical yield appeared to increase by lowering the reaction temperature (Table II, entries 3–6). (3) The sense and extent of the asymmetric induction is highly dependent on the nature of the added second hydroxylic compound, R′OH. Interestingly, reversal in the sense of differentiation occurred by changing the R′O group from simple alkoxyl (entries 1–8) to β,β,β-trifluoroethoxyl or 2,6-di-*tert*-butylphenoxyl (entries 9 and 11). (4) The reagent prepared from equimolar amounts of (*R*)-(+)-**1** and AlH_3 gave only a low optical yield (entry 13).

Complex hydride reagents of type $LiAlH_n(OR')_{4-n}$ are known to exist in a complicated equilibrium with a variety of disproportionated and aggregated species.[14] However, the stereochemical outcome arising from the rigid, unique chiral conformation of the present reagent is most economically rationalized by the mechanism involving a six-membered, chelating transition state.[15] In the transition state of the reaction of acetophenone and (*R*)-**2** containing an ordinary R′ group, the R′O oxygen acts as the bridging atom because of its highest basicity among the three oxygens attached to Al. Therefore, the chair conformation with axial-methyl and equatorial-phenyl groups,[16] **4**, is favored over the diastereomeric transition



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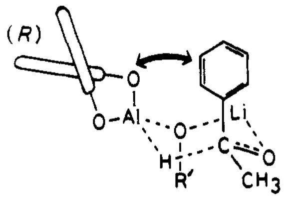

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state **5**, in accord with the observed enantioselectivity. The origin of the unusual enantioselection with the reagent bearing β,β,β-trifluoroethoxy or a bulky aryloxy group remains unclear.[17] Electronic effects of phenyl group on the stability of the transition state are also to be clarified.

Acknowledgment. Partial financial support from the Ministry of Education, Japanese Government (Grant-in-aid, No. 303023), is acknowledged.

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(5) Aging time (1–10 h) did not affect the enantioselectivity.
(6) The salt was recrystallized repeatedly from acetone–hexane until a constant specific rotation, $[\alpha]^{22}{}_D$ −10.4 (*c* 1.08, ethanol), was obtained.
(7) The synthetic and resolved materials were purified under identical GLC conditions. Both samples were alternately subjected to the measurement of optical rotation under the *same conditions* (solvent source, concentration, temperature, etc.) using a JASCO DIP-SL automatic polarimeter and a 0.1-dm quartz cell. The reported highest $[\alpha]_D$ value (temperature unstated) is given in footnote *n* of Table I. Recorded mp 48–49 °C: Kenyon, J.; Partridge, S. M. *J. Chem. Soc.* **1936,** 128.
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(11) For an enantioselective reduction of benzaldehyde-α-*d*, see Midland, M. M.; Tramontans, A.; Zderic, S. A. *J. Am. Chem. Soc.* **1977**, *99*, 5211.
(12) 2-Octanone formed 2-octanol in 24% ee. Benzyl methyl ketone gave 1-phenyl-2-propanol in 13% ee.
(13) A mixture of **2** ($R'O = C_2H_5O$) and propiophenone (1:1 ratio) in THF was stirred at 30 °C, and the reaction was monitored by analyzing the aliquots (quenched by dilute HCl) by GLC. After the ratio of the unreacted ketone to ethylphenylcarbinol had become constant (23:77) (the reaction stopped at this stage! (cf. Meyers, A. I.; Kendall, P. M. *Tetrahedron Lett.* **1974,** 1337)), acetophenone was added and the mixture was allowed to stand at 30 °C. Upon quenching of the mixture with CH_3OH, 0.14 equiv of H_2 was evolved. No methylphenylcarbinol was formed, however, indicating the irreversible nature of the reaction. This result was reproducible.
(14) Reaction of acetophenone and a reagent formed from equimolar amounts of $LiAlH_4$ and (*R*)-(+)-**1** without any added R′OH (30 °C, THF) afforded (*R*)-(+)-**3** ($R = CH_3$) in only 2% ee. In this case, $LiAlH_4$ is probably the major reducing agent.
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(16) Models suggest the existence of severe steric repulsion between the axial group and binaphthoxy oxygen and C-3 hydrogen.
(17) In such cases, owing to the decrease in the basicity of the R′O oxygen and/or steric constraints, the preferred transition state may adopt a binaphthoxy oxygen as the chelating atom, consistent with the experimental results.

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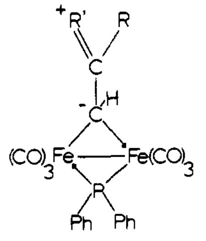
Triangular Iron–Silver Clusters

Sir:

Despite recent activity in the metal cluster field,[1] relatively few systematic methods are available for the introduction of a metal fragment into a bi- or polynuclear framework.[2,3] Thus, for example, mixed metal clusters in which a group 1b element, Cu, Ag, or Au, is part of a cluster polyhedron[4] are rare although there is evidence that these metals, especially gold,[5] have a propensity to form stable clusters. We describe here a simple and possibly versatile route to clusters containing silver and iron group atoms, which involves the addition of hydrocarbon soluble silver salts to neutral binuclear iron carbonyl complexes. In these reactions the d^{10} silver ion can be regarded as a Lewis acid, interacting with an electron-rich metal carbonyl species. This approach is thus the reverse of that recently described by Stone and co-workers[6] where the electronically unsaturated transition metal carbonyl complex $Os_3(CO)_{10}H_2$ was used as an electrophilic center for attack by nucleophilic d^{10} Ni, Pt, and Au compounds.

The compounds I (R = Ph; R′ = NMe_2, NEt_2, $NPr_2{}^n$, NHMe, NHEt, NHC_6H_{11}-c, NC_5H_{10}-c, NHPh) can be synthesized in high yield via the addition of primary or secondary amines across the triple bond of the σ,π-acetylide in II. Treatment of I (R = Ph; R′ = NHMe) in benzene with an equimolar quantity of silver perchlorate in benzene afforded (90%) an immediate crystalline precipitate of an adduct $Fe_2(CO)_6[CHC(R)R'](PPh_2)AgClO_4$ (III, R = Ph; R′ = NHMe): mp 147 °C dec; ν(CO) (THF) 2034 (m), 1991 (s), 1955 (m, br), 1940 (m, br) cm^{-1}. The complex is indefinitely stable in air in the solid state, insoluble in petroleum ether, sparingly soluble in toluene, and very soluble in tetrahydrofuran. Solutions in tetrahydrofuran are stable for several hours under nitrogen. The ^1H NMR spectrum of III (acetone-d_6, 60 MHz) (δ (wrt Me_4Si) 2.75 (s, C–H), 3.05 (d, J = 10 Hz, CH_3), 6.7–7.3 (m, C_6H_5)) was very similar to that of I (C_6D_6) (1.65 (s, C–H), 1.80 (d, J = 6 Hz, CH_3), 6.7–7.3 (m, C_6H_5)) except for a marked downfield shift of the –CH and CH_3 resonances. In neither case was the coupled N-H resonance observable. The ^{31}P spectrum at 183 K showed two doublets (δ (85% H_3PO_4) 173.4 ppm ($^2J_{^{107}Ag\text{-}P} = 28.22$, $^2J_{^{109}Ag\text{-}P} = 32.40$ Hz) due to coupling of phosphorus with the magnetic silver nuclei ^{107}Ag and ^{109}Ag of spin ½. At 300 K, a broad doublet, with an average Ag–^{31}P coupling was observable probably owing to solvent exchange processes at the coordinated silver atom. Structural details were revealed by a single-crystal X-ray analysis. Red prisms of $Fe_2(CO)_6[CHC(Ph)NHMe]$-$(PPh_2)AgClO_4{\cdot}C_6H_6{\cdot}C_6H_5Me$ crystallize in the triclinic space group $P\bar{1}$ with a = 14.101 (3), b = 10.654 (4), c = 15.777 (4) Å; α = 93.68 (4), β = 114.27 (2), γ = 95.03 (3)°. With Z = 2 and a molecular weight of 974.71 the calculated density of



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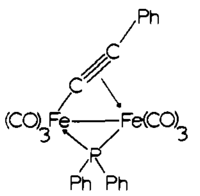

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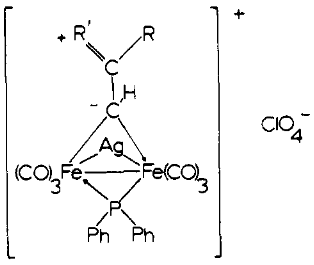

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