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Heterometallic Alkylidyne Clusters: Natural Products as Sources of Chirality

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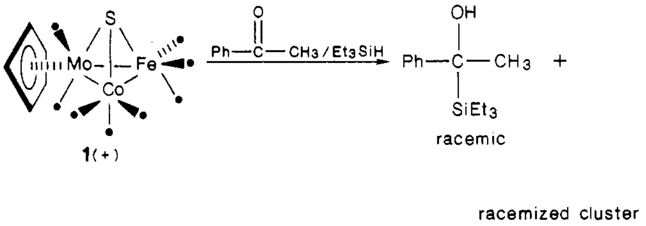
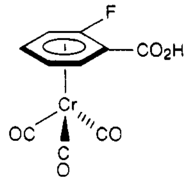
A series of mixed-metal clusters of the type $MCo_2(CO)_6CCO_2$(menthyl), where M = $Co(CO)_3$, $(C_5H_5)Mo(CO)_2$, $(i\text{-}PrC_5H_4)Mo(CO)_2$, or (indenyl)$Mo(CO)_2$, have been synthesized and characterized by using FAB mass spectrometry and 2D NMR techniques. Treatment of the tricobalt cluster with $Ph_2AsCH_2CH_2PPh_2$ yields a pair of diastereomers which are interconverted via migration of the Ph_2As terminus of the arphos ligand from one cobalt vertex to another. This process has been followed by variable-temperature ^{31}P NMR spectroscopy and has a barrier of $\approx$13 kcal mol^{-1}. When M $\neq$ $Co(CO)_3$, the two remaining cobalt vertices are diastereotopic and are, in principle, not equally susceptible to attack by an incoming ligand. To test for chiral discrimination, these molecules have been treated with phosphines of widely differing cone angles. For trimethyl phosphite, there is very little selectivity but with tricyclohexylphosphine the two diastereomers are formed in a 75:25 ratio.

Introduction

Implicit in the assumption that metal clusters will eventually provide a bridge between homo- and heterogeneous catalytic systems is the belief that a process which is truly cluster-catalyzed should be capable of generating chiral products when the cluster itself is asymmetric. Attempts to provide such verification via the attempted hydrosilylation of a ketone using a chiral cluster, **1**, led to a racemic product;[1] it was subsequently established that the cluster itself lost its stereochemical integrity during the course of the reaction. More recently, Vahrenkamp has unequivocally demonstrated that substitutions in phosphine-capped trimetallic tetrahedral systems can proceed via mechanisms which involve opening up the cluster framework with subsequent carbonyl elimination and cluster re-formation.[2]



In some ways, catalysis with chiral clusters has followed the path of the optically active (arene)ML_n complexes which were originally prepared with the goal of hydrogenating prochiral olefins.[3] An early approach was to synthesize $(\eta^6\text{-}C_6H_4XY)Cr(CO)_3$ complexes in which the initially achiral arene was rendered asymmetric by the π-complexation of the tripodal metal fragment onto a face of the ligand. Of course, one obtains a racemic mixture which, in principle, is separable by, for example, treatment of a carboxylic acid derivative, **2**, with a naturally occurring alkaloid base such as strychnine or brucine.[4] Many chiral half-sandwich complexes have now been synthesized by using this approach. Unfortunately, during the catalytic hydrogenation process, the arene is displaced and so all potential asymmetric induction is lost. To overcome this problem, it was necessary to position the central metal atom itself in a chiral environment, as in **3**.[5]



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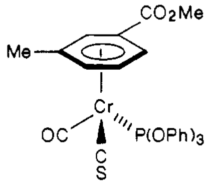

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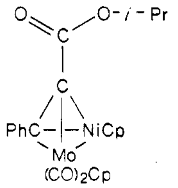
Following the pioneering methods of Vahrenkamp[6] or of Stone,[7] it is now relatively straightforward to construct tetrahedral clusters comprised of four different vertices, as in **4** or **5**. However, there remains the major problem of enantiomer separation; fortunately, on some occasions, spontaneous resolution occurs upon crystallization. Nevertheless, under the reaction conditions which might be expected to yield chiral catalysis, small mixed-metal clusters can racemize by a variety of methods. A common route is that of cluster opening to allow coordination of an extra carbon monoxide ligand.[2] Furthermore, it has been demonstrated that, in some cases, cluster fluxionality is not restricted merely to migration of the peripheral ligands but that the metal vertices themselves can be interchanged.[8,9]



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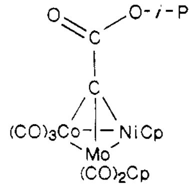

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A second approach is to incorporate a nonsymmetrical bidentate ligand into the cluster so as to render the molecule asymmetric, as in **6**. This is a chemically much simpler method that permits the facile synthesis of chiral clusters on a relatively large scale, but it also has its disadvantages. Again, one is faced with a potentially severe enantiomer separation problem, but an even more fun-

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(1) Pittman, C. U., Jr.; Richmond, M. G.; Absi-Halabi, M.; Beurich, H.; Richter, F.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 786.

(2) Planalp, R. P.; Vahrenkamp, H. *Organometallics* **1987**, *6*, 492.

(3) Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 151.

(4) Dabard, R.; Jaouen, G. *Tetrahedron Lett.* **1969**, *39*, 3391.

(5) Simonneaux, G.; Meyer, A.; Jaouen, G. *J. Chem. Soc., Chem. Commun.* **1975**, 69.

(6) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169.

(7) Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89.

(8) Mlekuz, M.; Bougeard, P.; Sayer, B. G.; Peng, S.; McGlinchey, M. J.; Marinetti, A.; Saillard, J.-Y.; Ben Naceur, J.; Mentzen, B.; Jaouen, G. *Organometallics* **1985**, *4*, 1123.

(9) D'Agostino, M. F.; McGlinchey, M. J. *Polyhedron* **1988**, *7*, 807.

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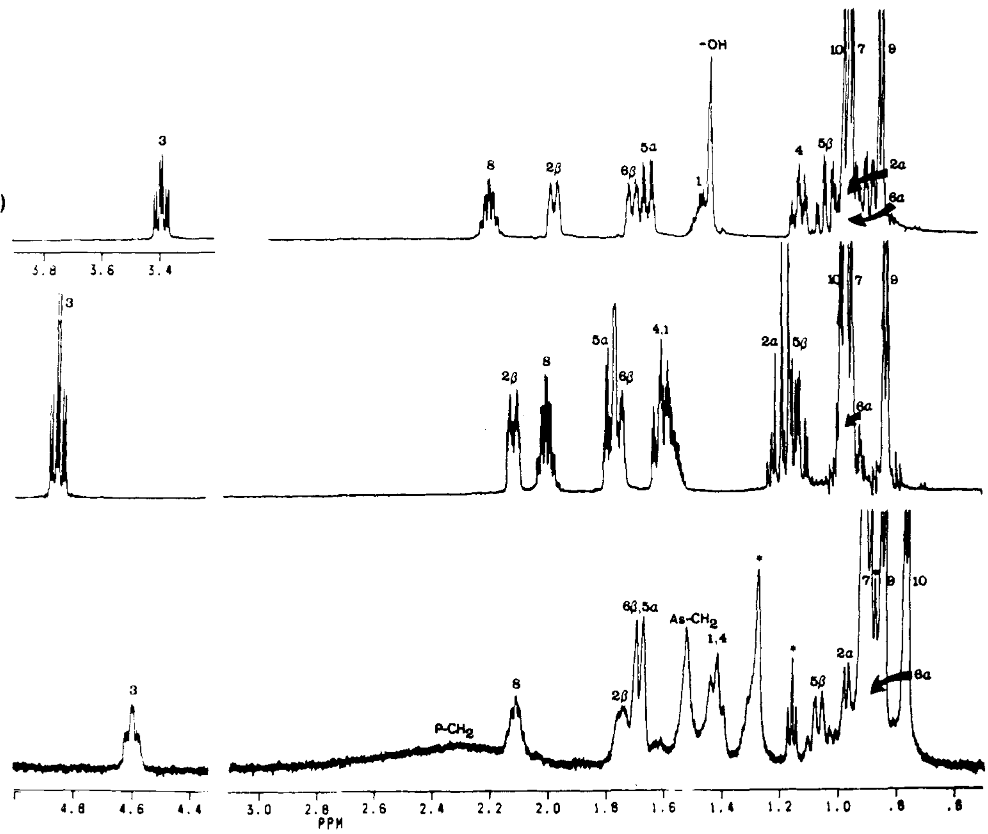
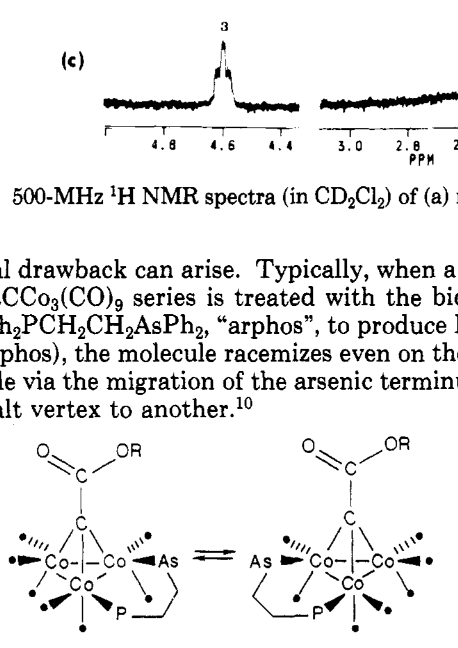


Figure 1. 500-MHz ^1H NMR spectra (in CD_2Cl_2) of (a) menthol, (b) menthyl trichloroacetate, and (c) $(menthyl)O_2CCCo_3(CO)_7(arphos)$ (**9**).

damental drawback can arise. Typically, when a cluster of the $RCCo_3(CO)_9$ series is treated with the bidentate ligand $Ph_2PCH_2CH_2AsPh_2$, "arphos", to produce $RCCo_3(CO)_7(arphos)$, the molecule racemizes even on the NMR time scale via the migration of the arsenic terminus from one cobalt vertex to another.[10]



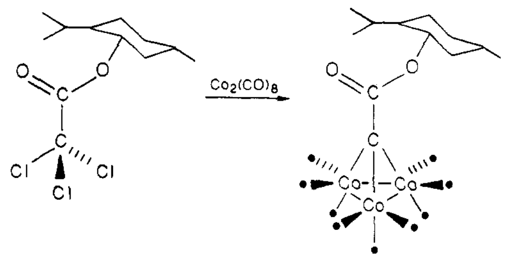
a **b**

6, R = *i*-Pr; **9**, R = menthyl

Another general route to the production of chiral clusters is the incorporation of a chiral natural product in the molecule, as in **7**. With this approach, the cluster produced is enantiomerically pure and thus there is no necessity for time-consuming separations. Recently, Vahrenkamp has prepared a series of chiral complexes containing the menthyl substituent, and, by further isolobal substitutions of $Co(CO)_3$ vertices by CpNi or $CpMo(CO)_2$ moieties, he has prepared and ultimately separated the resulting diastereomers.[11] This prompts us to report our own data on a closely related set of clusters in which we have not only built a menthyl substituent into the tricobalt nonacarbonyl starting material but have also incorporated several NMR probes to monitor the stereochemical course of succeeding reactions.

Results and Discussion

The most general route to the $RCCo_3(CO)_9$ series of clusters is via the reaction of dicobalt octacarbonyl with the appropriate $RCCl_3$ precursor.[12] With the intention of generating a chiral cluster on a large scale, (+)-menthol was converted to its trichloroacetate ester and the product treated with $Co_2(CO)_8$. This molecule has also been synthesized by Vahrenkamp.[11] The resulting cluster is, of course, chiral, but its source of chirality is located in the organic substituent and at this stage there is no differentiation between the metal vertices since they are equilibrated via rotation about the apical carbon–ester carbon bond; this parallels the situation for methyl groups in chiral molecules.



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The apparent complexity of the ^1H NMR spectrum of the menthyl groups is readily overcome by the use of two-dimensional techniques at high magnetic field. Figure 1 depicts the 500-MHz ^1H NMR spectrum of (+)-menthol itself as well as those of the trichloroacetate ester and of the arphos cluster **9**. The assignments were obtained by using the two-dimensional NMR pulse sequences for the ^1H–^1H COSY and ^1H–^{13}C shift-correlated experiments.[13]

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[10] Sutin, K. A.; Kolis, J. W.; Mlekuz, M.; Bougeard, P.; Sayer, B. G.; Quilliam, M. A.; Faggiani, R.; Lock, C. J. L.; McGlinchey, M. J.; Jaouen, G. *Organometallics* **1987**, *6*, 439.

[11] Blumhofer, R.; Vahrenkamp, H. *Chem. Ber.* **1986**, *119*, 683.

[12] Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97.

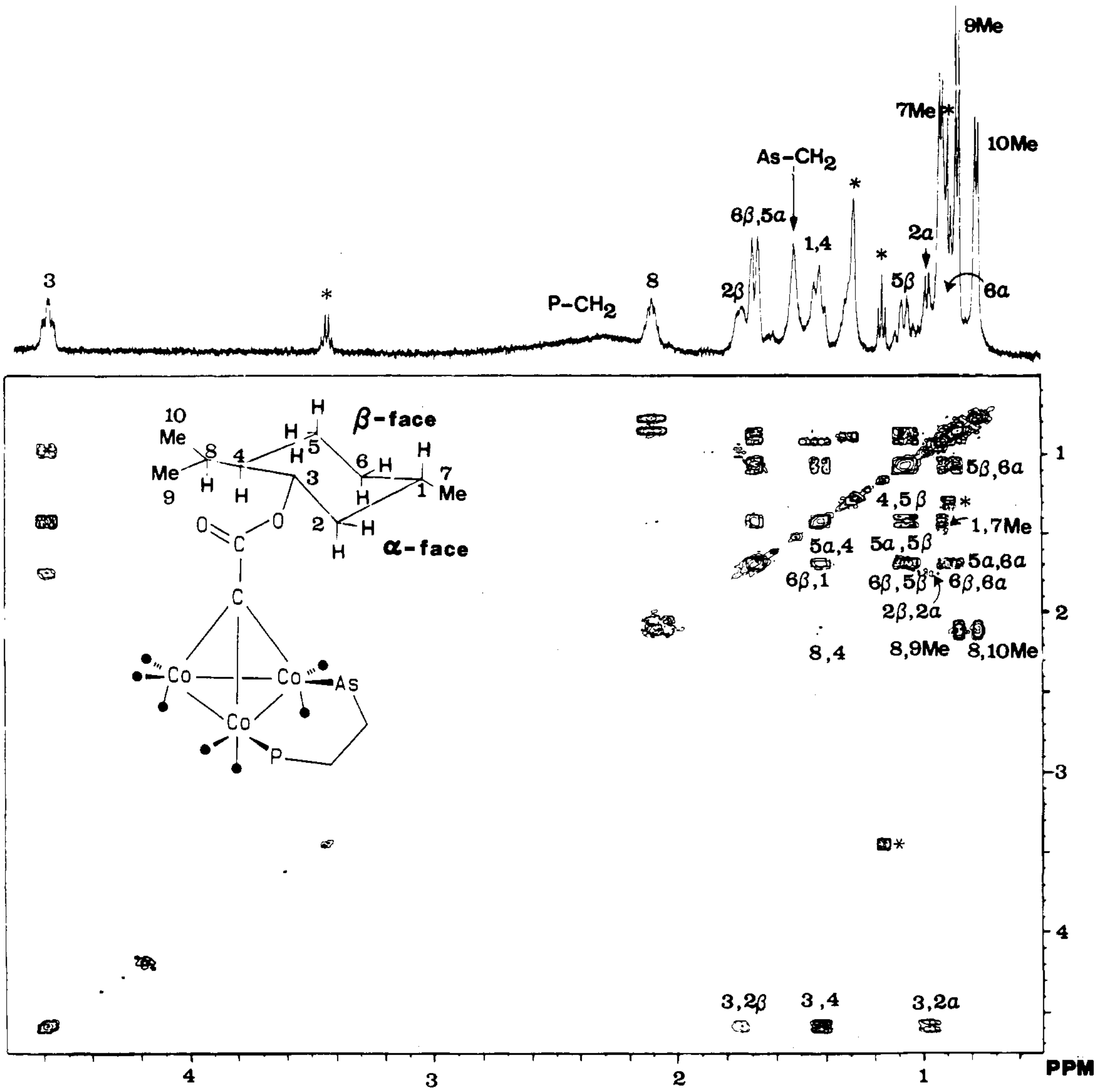
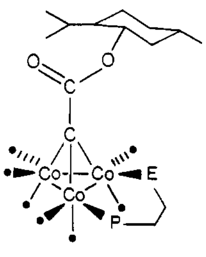


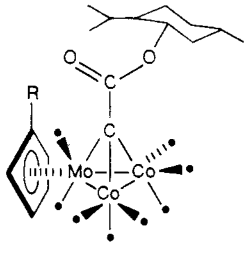
Figure 2. 500-MHz two-dimensional ^{1}H–^{1}H COSY NMR spectrum of (menthyl)$O_2CCCo_3(CO)_7$(arphos) (9). (Peaks marked with an asterisk are assignable to ether and other solvent impurities.)

In the former case, the data are presented as a contour map with the normal one-dimensional spectrum lying along the diagonal while proton resonances related by spin–spin couplings exhibit off-diagonal peaks; a typical spectrum is shown in Figure 2. In principle, one could use these shift data to evaluate the diamagnetic anisotropy of the cobalt carbonyl ligands, as we have done previously with $Cr(CO)_3$ ligands bonded to steroidal hormones,[14] but at this time we defer such calculations to another paper.

Treatment of 7 with $Ph_2PCH_2CH_2PPh_2$ (diphos) yields the complex (menthyl)$O_2CCCo_3(CO)_7$(diphos) (8) in which the $Co(CO)_2P$ vertices are now diastereotopic and should thus exhibit two resonances in the ^{31}P NMR spectrum. One does indeed obtain a spectrum exhibiting two phosphorus environments, although the peaks are somewhat broadened at room temperature. As has been observed by Aime et al. for cobalt clusters containing chemically different ^{31}P nuclei,[15] these resonances sharpen noticeably at low temperatures (see Figure 3). This broadness is not a chemical exchange process but instead can be attributed to quadrupolar effects because of the proximity of the ^{59}Co nuclei which have $I = ^7/_2$. As is common with phosphine complexes, there is a noticeable dependence of ^{31}P chemical shifts with temperature. In 8 the two ^{31}P peaks are well separated. Thus, clearly, in a cluster of the type $R^*CCo_2(CO)_6ML_n$ (where R* is a chiral group) in which the cobalt vertices are diastereotopic, it would be possible to see whether attack by a monodentate phosphine has occurred to an equal extent at both cobalt sites. We shall return to this point presently. In a similar fashion, the reaction of 7 with arphos yields (menthyl)$O_2CCCo_3(CO)_7$(arphos) (9). At room temperature, the phosphorus-31 NMR spectrum is a singlet, but, upon cooling to −50 °C, it appears as a doublet. The variable-temperature ^{31}P



8, E = PPh_2
9, E = $AsPh_2$



10, R = H
11, R = *i*-Pr

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(13) Benn, R.; Guenther, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 350.

(14) McGlinchey, M. J.; Burns, R. C.; Hofer, R.; Top, S.; Jaouen, G. *Organometallics* **1986**, *5*, 104.

(15) Aime, S.; Botta, M.; Gobetto, R.; Osella, D.; Milone, L. *Gazz. Chim. Ital.* **1987**, *117*, 773.

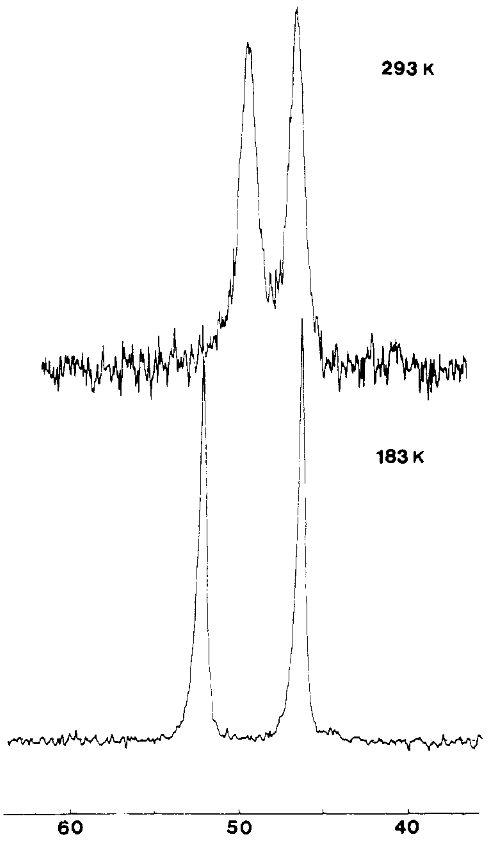

Figure 3. 101.2-MHz variable-temperature ^{31}P NMR spectra of (menthyl)$O_2CCCo_3(CO)_7$(diphos) (8) showing the clear differentiation of the diastereotopic phosphorus nuclei.

spectra are shown in Figure 4 and exhibit a coalescence pattern; the limiting spectrum reveals a peak separation of 410 Hz, and this, in conjunction with a coalescence temperature of 288 K, yields an approximate activation energy barrier of 13.1 ± 0.5 kcal mol^{-1}. This coalescence behavior is readily explicable in terms of interconversion of the two diastereomers **9a** and **9b**. As discussed above, ^{31}P nuclei bonded to the diastereotopic cobalt atoms resonate at different frequencies and thus two absorptions are observed when the migration of the arsenic terminus is slow on the NMR time scale. The measured barrier of $\approx$13 kcal mol^{-1} for the interconversion of the diastereomers **9a** and **9b** compares very favorably with the reported activation energy (13.1 ± 0.5 kcal mol^{-1}) for the racemization of $Me_2CHO_2CCCo_3(CO)_7$(arphos) which was monitored by using the ^1H and ^{13}C NMR resonances of the isopropyl methyl signals;[10] apparently, the same mechanism is operative.

Another method of rendering two cobalt vertices diastereotopic is to introduce a different metal vertex in the third position. This is readily accomplished by treatment of **7** with $[C_5H_5)Mo(CO)_3]_2$ to give **10**—a reaction previously reported by Vahrenkamp.[11] However, we wished to build into the cluster a probe for chirality so that the formation of diastereomers could be detected. To this end, we replaced the Cp in the $(C_5H_5)Mo(CO)_2$ group by the isopropylcyclopentadienyl ligand, $C_5H_4CHMe_2$. This moiety is obtained in good yield by the reaction of 6,6-dimethylfulvene with $Mo(CO)_6$ in high-boiling petroleum ether[16] and, after reaction with **7**, ultimately yields the cluster **11**. The ^{13}C NMR spectrum of **11** exhibits five methyl resonances, and these are assignable to the methyl group at C-1 of the menthyl substituent, the diastereotopic methyls of the isopropyl group at the menthyl C-4 position, and finally the diastereotopic methyls of the isopropylcyclopentadienyl ligand.

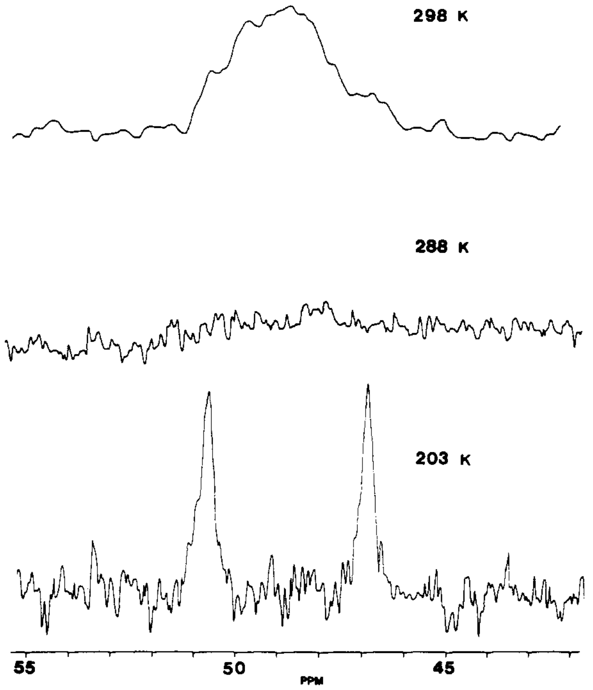

Figure 4. 101.2-MHz variable-temperature ^{31}P NMR spectra of (menthyl)$O_2CCCo_3(CO)_7$(arphos), showing the slow interconversion of the diastereomers **9a** and **9b** at low temperature.

As discussed above, incorporation of arphos into these chiral clusters brings about formation of diastereomers, and, in this case, the two isomers are approximately 50/50. In the tricobalt cluster **9** rapid interconversion of the diastereomers is possible via migration of the diphenylarsenido terminus from one cobalt to another; thus, one sees a single ^{31}P signal at room temperature and two peaks at low temperature. In contrast, when the third metal vertex is occupied by a (cyclopentadienyl)dicarbonylmolybdenum fragment, as in **10**, migration of the arsenic ligand is blocked.[10] Thus, treatment of the chiral cluster *i*-$PrCpMoCo_2(CO)_8CCO_2$(menthyl) (**11**) with arphos yields the corresponding complex **12** in which two equatorial cobalt carbonyls are replaced. Now the ^{31}P NMR spectrum of this noninterconverting diastereomeric mixture shows two peaks at all temperatures.

It is well established that replacement of the η^5-cyclopentadienyl ligand by the indenyl group leads to enhanced rates of substitution at the metal center;[17] this has been attributed to the ability of the indenyl moiety to slip from an η^5- to an η^3-bonding mode.[18] However, there is another advantage to be gained by using C_9H_7 rather than C_5H_5 as a ligand, that is, the reduced symmetry of the former (C_s) relative to the latter (C_{5v}) allows one to detect chirality

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[16] Abel, E. W.; Singh, A.; Wilkinson, G. *J. Chem. Soc.* **1960**, 1321.

[17] (a) Rerek, M. E.; Ji, L.-N.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1983**, 1208. (b) Ji, L.-N.; Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 740.

[18] (a) White, C.; Mawby, R. J. *Inorg. Chim. Acta* **1970**, *4*, 261. (b) Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 648. (c) Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 962. (d) Casey, C. P.; O'Connor, J. M. *Organometallics*, **1985**, *4*, 384. (e) Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* **1985**, *4*, 929 and references therein. (f) Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839. (g) Eshtiagh-Hosseini, H.; Nixon, J. F. *J. Less-Common Met.* **1978**, *61*, 107. (h) Mlekuz, M.; Bougeard, P.; Sayer, B. G.; McGlinchey, M. J.; Rodger, C. A.; Churchill, M. R.; Ziller, J. W.; Kang, S.-K.; Albright, T. A. *Organometallics* **1986**, *5*, 1656. (i) Marder, T.; Calabrese, J. C.; Roe, D. C.; Tulip, T. H. *Organometallics* **1987**, *6*, 2012.

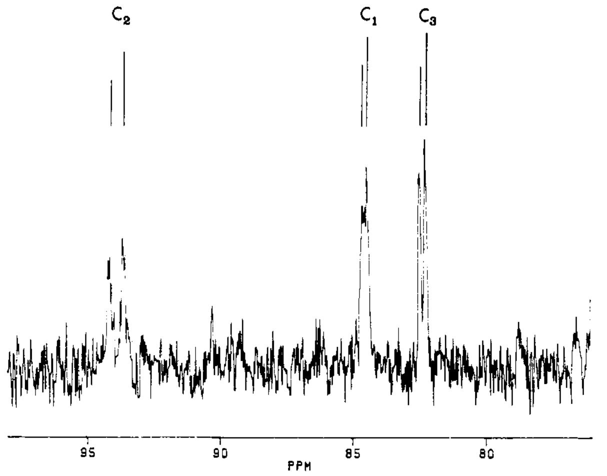
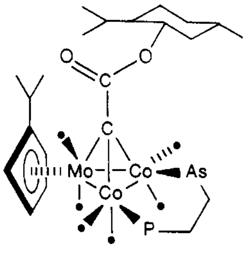


Figure 5. Section of the 125-MHz ^{13}C NMR spectrum of the diastereomers of (indenyl)Mo(CO)$_2$Co$_2$(CO)$_4$(arphos)CCO$_2$(menthyl) (**14** and **15**) showing the further splitting of the indenyl five-membered ring carbons.

in a molecule since the indenyl ligand possesses three pairs of potentially diastereotopic protons as well as four carbon-13 pairs. In practice, the C-1 and C-3 positions in the five-membered ring are the most useful since they are the closest to the metal and also bear protons which, by virtue of their nuclear Overhauser effect, enhance the sensitivity of the ^{13}C signals. We have previously utilized this property of indenyl groups to show that the C_8H_9 ligand produced by protonating (indenyl)Rh(C_8H_8) adopts a chiral conformation.[19] The cluster obtained by reacting **7** with [(indenyl)Mo(CO)$_3$]$_2$ does indeed exhibit three ^{13}C resonances for the proton-bearing carbons of the five-membered ring of the indenyl ligand. The peaks in the molybdenum dimer starting material are at 93.4 (C-2) and 84.1 ppm (C-1,3); in the cluster **13**, these resonances are at 92.8, 84.0, and 82.1 ppm. It is thus clear that use of an indenyl rather than a Cp group is doubly advantageous.



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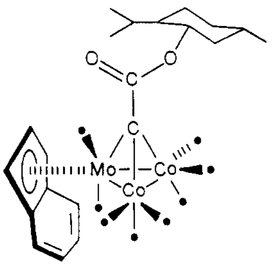

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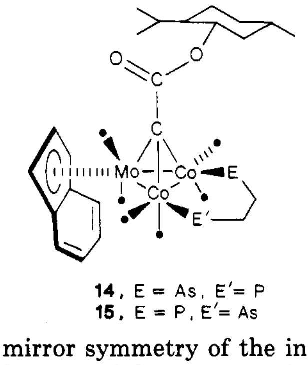

14, E = As, E′= P
15, E = P, E′= As

In **13** the mirror symmetry of the indenyl ligand has been broken because of the presence of the chiral capping group, and this caused a doubling of the previously equivalent C-1 and C-3 nuclei *within the same molecule*.

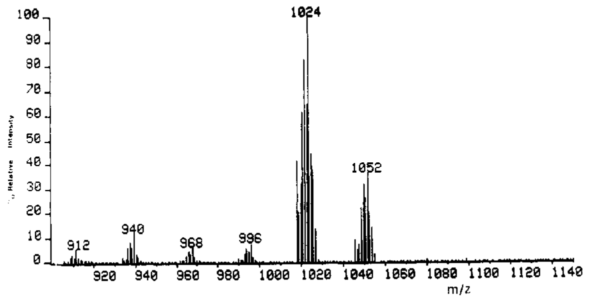

Figure 6. High mass region of the FAB mass spectrum of (indenyl)Mo(CO)$_2$Co$_2$(CO)$_4$(arphos)CCO$_2$(menthyl) (**14**/**15**). The peak at *m*/*z* 1052 corresponds to the [P − 3CO]$^+$ ion.

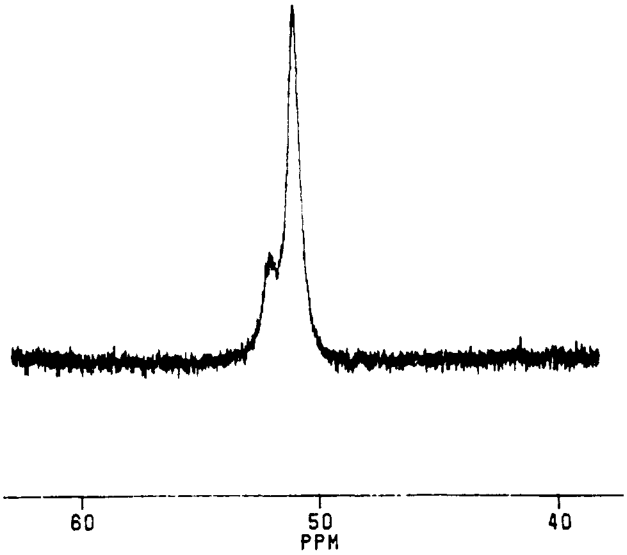

Figure 7. 202.4-MHz ^{31}P NMR spectrum of (menthyl)O$_2$CCCo$_3$(CO)$_8$[P(C$_6$H$_{11}$)$_3$] (**17**) showing the 1:3 ratio of diastereomers.

Now incorporation of an arphos ligand brings about a further splitting of these peaks as well as for the C-2 resonance. This comes about because the arphos can bind in two ways, as in **14** and **15**, thus yielding a diastereomeric mixture in the ratio 54/46 as indicated by the ^{13}C NMR spectrum shown in Figure 5. As a routine part of the characterization of all these clusters, their FAB mass spectra were recorded and a typical spectrum appears as Figure 6.

The presence of a pair of diastereotopic cobalt vertices in a cluster suggests that it may be possible to bring about preferential attack at a single vertex. If such a reaction could be carried out with 100% efficiency, then it would be analogous to the reaction of an enzyme specifically with only one of the enantiotopic hydrogens of a methylene group. In a preliminary test of the viability of such a process, we allowed the cluster **10** to react with 1 mol of trimethyl phosphite to give **16**; the resulting mixture of diastereomers exhibits in the ^{31}P NMR two resonances of approximately equal area. In contrast, use of a very bulky ligand, viz., tricyclohexylphosphine, yields **17**. If the reaction were to proceed with any degree of selectivity, the phosphorus-31 NMR spectrum of the product ought to show resonances of unequal intensity. Gratifyingly, as shown in Figure 7, the 202.4-MHz ^{31}P spectrum of the cluster shows two resonances at chemical shifts appropriate for phosphines bonded to cobalt and in an integrated ratio of 75/25. We prefer not to speculate as to the detailed structures of these isomers of **17** until we have crystallographic data. It is anticipated that use of a bulky and chiral phosphine will yield essentially a single optically

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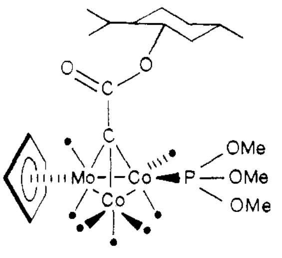
[19] Clark, D. T.; Mlekuz, M.; Sayer, B. G.; McCarry, B. E.; McGlinchey, M. J. *Organometallics* 1987, *6*, 2201.

pure product and establishment of the absolute configuration will be straightforward since the configuration of the menthyl substituent is already known.



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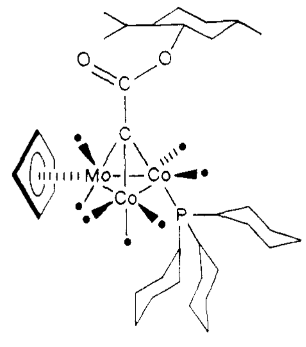

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To conclude, it has been shown that chiral tetrahedral clusters containing three metal vertices can be obtained by incorporating a (+)-menthyl ester at the apical position. Reactions with mono- or diphosphines can lead to diastereomers whose formation can be monitored by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. A method is proposed by which optically pure clusters may be obtainable in good yields without recourse to time-consuming diastereomer separations. Future reports will describe clusters derived from *exo*-borneol, *endo*-borneol, and related systems.

Experimental Section

All preparations were carried out under an atmosphere of dry nitrogen. Solvents were dried according to standard procedures. Infrared spectra were recorded on a Perkin-Elmer 283 instrument using NaCl plates. Fast atom bombardment (FAB) mass spectra were obtained on a VG analytical ZAB-SE spectrometer with an accelerating potential of 8 kV and a resolving power of 10 000. NBA was used as the sample matrix and Xe as the bombarding gas. NMR spectra were obtained by using a Bruker AM 500 or a WM 250 spectrometer. ^{1}H and ^{13}C chemical shifts are reported relative to tetramethylsilane; ^{31}P chemical shifts are quoted relative to 85% H_3PO_4. Microanalytical data are from the Guelph Chemical Laboratories, Guelph, Ontario, Canada.

$Co_3(CO)_9CCO_2$(menthyl)[11] (7), [Mo(CO)$_3$(*i*-PrCp)]$_2$,[16] [Mo(CO)$_3$(C_9H_7)]$_2$,[20] and $CpMoCo_2(CO)_8CCO_2$(menthyl)[11] (10) were prepared by published methods.

($Ph_2PCH_2CH_2PPh_2$)$Co_3(CO)_7CCO_2$(menthyl) (8). A solution of 7 (1.030 g, 1.65 mmol) and diphos (0.6396 g, 1.61 mmol) in THF (65 mL) was stirred at reflux for 10 min and then at room temperature for a further 30 min. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 20/80) which showed the formation of 8 as a green spot (R_f 0.10). Chromatography on silica gel (eluent, ether/hexane, 20/80) gave dark green crystals of 8 (0.5135 g, 0.53 mmol, 33%): mp 85–87 °C; ^{13}C NMR (CD_2Cl_2) δ 205.2 (cobalt carbonyls), 182.1 (ester carbonyl), 132.8, 131.2, 130.2, 128.6 (phenyl carbons), 74.9 (C-3), 47.7 (C-4), 41.3 (C-2), 34.6 (C-6), 31.8 (C-1), 25.8 (C-8), 25.4 (CH_2P), 23.1 (C-5), 22.0 (C-7), 20.8 (C-10), 15.8 (C-9); ^{31}P NMR (CD_2Cl_2, 306 K) 49.3 and 46.8 ppm; IR (CH_2Cl_2) ν_{CO} 2050 (s), 2000 (vs), 1985 (sh), 1960 (sh), 1645 (ester) cm^{-1}; FAB mass spectrum, *m/z* (relative intensity) 938 (2, (M – CO)$^+$), 882 (41, (M – 3CO)$^+$), 854 (4, (M – 4CO)$^+$); 826 (21, (M – 5CO)$^+$), 798 (26, (M – 6CO)$^+$), 771 (21, (M – 7CO)$^+$), 643 (11, ($C_{29}H_{24}O_2Co_3P_2$)$^+$, 616 (100, ($C_{28}H_{25}OCo_3P_2$)$^+$, 588 (85, ($C_{27}H_{25}Co_3P_2$)$^+$), 560 (27, ($C_{25}H_{21}Co_3P_2$)$^+$), 482 (24, ($C_{19}H_{15}Co_3P_2$)$^+$), 406 (58, ($C_{13}H_{11}Co_3P_2$)$^+$), 328 (25, ($C_7H_5Co_3P_2$)$^+$). Anal. Calcd for $C_{45}H_{43}O_9Co_3P_2$: C, 55.92; H, 4.69. Found: C, 55.70; H, 4.44.

($Ph_2AsCH_2CH_2PPh_2$)$Co_3(CO)_7CCO_2$(menthyl) (9). A solution of 7 (0.4429 g, 0.71 mmol) and arphos (0.2862 g, 0.65 mmol) in THF (35 mL) was stirred at 40 °C for 15 min and then at room temperature for a further 30 min. The progress of the reaction was followed by TLC on Kieselgel (eluent, ether/hexane, 15/85) which revealed the formation of 9 (R_f 0.39) as a dark green spot. Flash chromatography on silica gel (eluent, ether/hexane, 15/85) gave dark green crystals of 9 (0.4524 g, 0.45 mmol, 69%): mp 81–84 °C; ^{1}H NMR (CD_2Cl_2) δ 7.6–7.4 (20 H, phenyls), 4.6 (1 H, H-3), 2.3 (br, 2 H, PCH_2), 2.1 (1 H, H-8), 1.75 (1 H, H-2β), 1.7 (2 H, H-6β,H-5α), 1.55 (2 H, $AsCH_2$), 1.4 (2 H, H-1β,H-4α), 1.1 (1 H, H-5β), 1.0 (1 H, H-2α), 0.95 (3 H, Me-7), 0.9 (1 H, H-6α), 0.9 (3 H, Me-9), 0.8 (3 H, Me-10); ^{13}C NMR (CD_2Cl_2) δ 204.7 (cobalt carbonyls), 131.7, 130.1, 129.8, 129.7, 128.8, 128.6, 128.5 (phenyl carbons), 74.7 (C-3), 47.5 (C-4), 41.0 (C-2), 34.4 (C-6), 31.6 (C-1), 25.7 (C-8), 25.6 (CH_2P), 22.9 (C-5), 21.9 (C-7), 21.0 (C-10), 20.7 (CH_2As), 15.7 (C-9); ^{31}P NMR (CD_2Cl_2, 300 K) 47.2 ppm; ^{31}P NMR (CD_2Cl_2, 193 K) 51.0 and 46.9 ppm; IR (CH_2Cl_2) ν_{CO} 2050 (s), 2005 (vs), 1980 (sh), 1960 (sh), 1640 (ester) cm^{-1}; FAB mass spectrum, *m/z* (relative intensity) 982 (5, $C_{44}H_{43}O_8Co_3PAs$ (M – CO)$^+$), 926 (60, M – 3CO)$^+$), 899 (8, (M – 4CO)$^+$), 870 (23, (M – 5CO)$^+$), 842 (16, (M – 6CO)$^+$), 815 (28, (M – 7CO)$^+$), 687 (15, ($C_{29}H_{24}O_2Co_3PAs$)$^+$), 660 (100, ($C_{28}H_{25}OCo_3PAs$)$^+$), 631 (37, ($C_{27}H_{24}Co_3PAs$)$^+$), 604 (72, ($C_{25}H_{21}Co_3PAs$)$^+$, 526 (65, ($C_{19}H_{15}Co_3PAs$)$^+$), 450 (74, ($C_{13}H_{11}Co_3PAs$)$^+$), 372 (37, ($C_7H_5Co_3PAs$)$^+$). Anal. Calcd for $C_{45}H_{43}O_9Co_3PAs$: C, 53.49; H, 4.29. Found: C, 53.59; H, 4.16.

(*i*-PrC_5H_4)$MoCo_2(CO)_8CCO_2$(menthyl) (11). [Mo(CO)$_3$(*i*-Pr-Cp)]$_2$ (0.3707 g, 0.64 mmol) and 7 (0.6573 g, 1.05 mmol) were heated under reflux in THF (35 mL) for 18 h. Progress of the reaction was followed by TLC on Kieselgel (eluent, ether/hexane, 4/96) showing a dark green spot, 11, at R_f 0.31. This green band was collected by flash chromatography on silica gel (eluent, ether/hexane, 3/97) yielding a dark green oil, 11, which solidified on standing at room temperature (0.2881 g, 0.39 mmol, 37%): decomp pt >170 °C; ^{13}C NMR (CD_2Cl_2) δ 210 (br, exchanging molybdenum and cobalt carbonyls), 180.0 (ester carbonyl), 93.2, 89.1 (CpCH's), 75.5 (C-3), 47.2 (C-4), 41.0 (C-2), 34.3 (C-6), 31.4 (C-1), 28.0 (Cp*C*HMe$_2$), 27.5 (CpCH*Me*), 26.0 (C-8), 23.3 (CpCH*Me*), 23.2 (C-5), 21.7 (C-7), 21.4 (C-10), 15.3 (C-9); IR (CH_2Cl_2) ν_{CO} 2090 (m), 2080 (m), 2035 (vs), 2025 (vs), 2010 (vs), 1995 (sh), 1920 (m), 1850 (m), 1730 (w), 1660 (ester) cm^{-1}; FAB mass spectrum, *m/z* (relative intensity) 801 (13, (M + 2CO)$^+$), 772 (34, (M + CO)$^+$), 742 (68, ((M)$^+$), 714 (32, (M – CO)$^+$), 686 (62, M – 2CO)$^+$), 658 (36, (M – 3CO)$^+$), 630 (60, (M – 4CO)$^+$), 602 (50, (M – 5CO)$^+$), 574 (100, (M – 6CO)$^+$), 546 (58, (M – 7CO)$^+$). Anal. Calcd for $C_{28}H_{30}O_{10}Co_2Mo$: C, 45.42; H, 4.08. Found: C, 45.30; H, 3.92.

(*i*-PrC_5H_4)$MoCo_2(CO)_6$(arphos)CCO_2(menthyl) (12). A solution of 11 (0.1175 g, 0.24 mmol) and arphos (0.1017 g, 0.23 mmol) in THF (10 mL) was stirred at ambient temperature for 20 min and then at reflux for 10 min. TLC on Kieselgel (eluent, ether/hexane, 5/95) showed the product 12 as a dark green spot at R_f 0.19. Chromatography on alumina gel (eluent, ether/hexane, 6/94) yielded green crystals of 12 (0.1297 g, 0.12 mmol, 50%): mp 163–166 °C; ^{31}P NMR (CD_2Cl_2, 300 K) 44.0 and 42.0 ppm; IR (CH_2Cl_2) ν_{CO} 2010 (s), 1980 (vs), 1975 (vs), 1970 (vs), 1945 (s), 1915 (m), 1635 (ester) cm^{-1}; FAB mass spectrum, *m/z* (relative intensity) 1044 (28, (M – 3CO)$^+$), 1016 (100, (M – 4CO)$^+$), 986 (5, (M – 5CO)$^+$), 960 (20, (M – 6CO)$^+$). Anal. Calcd for $C_{52}H_{54}O_8Co_2MoAsP$: C, 55.43; H, 4.83. Found: C, 55.27; H, 5.06.

(C_9H_7)$MoCo_2(CO)_8CCO_2$(menthyl) (13). [Mo(CO)$_3$(C_9H_7)]$_2$ (0.5381 g, 0.912 mmol) and 7 (0.7726 g, 1.24 mmol) were heated under reflux in THF (35 mL) for 14 h and then stirred at ambient temperature for 24 h. The reaction was followed by TLC on Kieselgel, showing the formation of a green product 13 at R_f 0.29 (eluent, ether/hexane, 5/95). The solvent was removed to leave a brown residue. Flash chromatography (eluent, ether/hexane, 5/95) yielded a dark green oil which solidified on standing at room temperature (0.1766 g, 0.24 mmol, 19%): decomp pt 155 °C; ^{13}C NMR (CD_2Cl_2) δ 210 (br, exchanging molybdenum and cobalt carbonyls), 127.5, 124.1 (indenyl aromatic CH's), 92.8 (indenyl C-2), 84.0, 82.1 (indenyl C-1, C-3), 75.7 (C-3), 47.4 (C-4), 41.2 (C-2), 34.2 (C-6), 31.7 (C-1), 25.8 (C-8), 23.0 (C-5), 21.8 (C-7), 20.8 (C-10), 15.6 (C-9); IR (CH_2Cl_2) ν_{CO} 2080 (m), 2070 (w), 2045 (s), 2020 (s), 2000 (s), 1945 (w), 1895 (w), 1720 (m), 1740 (sh), 1660 (ester) cm^{-1}; FAB mass spectrum, *m/z* (relative intensity) 750.82 (16, (M)$^+$), 692 (7, (M – 2CO)$^+$), 666 (11, (M – 3CO)$^+$), 638 (9, (M – 4CO)$^+$), 610 (42, (M – 5CO)$^+$), 582 (100, (M – 6CO)$^+$), 554 (51, (M – 7CO)$^+$). Anal. Calcd for $C_{29}H_{26}O_{10}Co_2Mo$: C, 46.55; H, 3.50. Found: C, 46.27; H, 3.26.

(C_9H_7)$MoCo_2(CO)_6$(arphos)CCO_2(menthyl) (14/15). A solution of 13 (0.1766 g, 0.24 mmol) and arphos (0.0870 g, 0.20

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[20] King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1965**, *4*, 475.

mmol) in THF (20 mL) was stirred at ambient temperature for 10 min and then at reflux for 40 min. The progress of the reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95), showing a yellow-green spot, **14**/**15** at R_f 0.10. Chromatography on alumina gel (eluent, ether/hexane, 20/80) yielded dark green crystals, **14**/**15** (0.1368 g, 0.12 mmol, 61%): decomp pt 118–120 °C; ^{13}C NMR (CD_2Cl_2) δ 211 (br, exchanging molybdenum and cobalt carbonyls), 181.8 (ester carbonyl), 141–124 (phenyls and indenyl aromatic CH's), 94.2/93.7 (indenyl C-2), 84.7/84.5, 82.5/82.3 (indenyl C-1, C-3), 75.2 (C-3), 47.6/47.1 (C-4), 41.5/41.1 (C-2), 34.8 (C-6), 32.0 (C-1), 26.0/25.9 (C-8), 25.4 (CH_2P), 23.7 (CH_2As), 23.2 (C-5), 22.3 (C-7), 20.8 (C-10), 16.3 (C-9); ^{31}P NMR (CD_2Cl_2, 300 K) 43.5 and 42.0 ppm; IR (CH_2Cl_2) ν_{CO} 2030 (w), 2010 (m), 1985 (vs), 1975 (vs), 1945 (m), 1910 (m), 1740 (sh), 1720 (s), 1635 (ester) cm^{-1}; FAB mass spectrum, *m*/*z* (relative intensity) 1052 (37, $(M - 3CO)^+$), 1024 (100, $(M - 4CO)^+$), 996 (7, $(M - 5CO)^+$), 968 (6, $(M - 6CO)^+$). Anal. Calcd for $C_{53}H_{50}O_8Co_2MoAsP$: C, 56.10; H, 4.44. Found: C, 56.36; H, 4.48.

$CpMoCo_2(CO)_7(P(OMe)_3)CCO_2$(menthyl) (16). A solution of **10** (0.184 g, 0.26 mmol) and trimethyl phosphite (0.032 mL, 0.26 mmol) was stirred together in THF (20 mL) for 47 h at room temperature. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 12/88) showing two spots: dark green **16**, R_f 0.29; green **10**, R_f 0.14. The solvent was removed and the resulting green oil separated by flash chromatography on silica gel (eluent, ether/hexane, 22/78). The product was obtained as a green oil, **16** (0.0836 g, 0.11 mmol, 42%): ^{31}P NMR (CD_2Cl_2, 300 K) 162.4 and 157.4 ppm; IR (CH_2Cl_2) ν_{CO} 2055 (s), 2000 (vs), 1990 (sh), 1970 (sh), 1920 (m), 1865 (m), 1655 (ester) cm^{-1}. The FAB mass spectrum indicates the presence of a very small amount of disubstituted product. FAB mass spectrum: *m*/*z* (relative intensity) 797 (12) $(M + 1)^+$), 768 (10, $(M - CO)^+$); 740 (14, $(M - 2CO)^+$); 712 (44, $(M - 3CO)^+$), 684 (71, $(M - 4CO)^+$), 656 (19, $(M - 5CO)^+$), 628 (65, $(M - 6CO)^+$), 600 (25, $(M - 7CO)^+$). $CpMoCo_2(CO)_6(P(OMe)_3)_2CCO_2$(menthyl): FAB mass spectrum, *m*/*z* (relative intensity) 836 (5, $(M - 2CO)^+$), 808 (7, $(M - 3CO)^+$), 780 (25, $(M - 4CO)^+$), 752 (4, $(M - 5CO)^+$), 724 (11, $(M - 6CO)^+$).

$CpMoCo_2(CO)_7(P(C_6H_{11})_3)CCO_2$(menthyl) (17). Tricyclohexylphosphine (0.0780 g, 0.28 mmol) and **10** (0.1825 g, 0.26 mmol) were stirred together in THF (20 mL) at ambient temperature for 38 h. The progress of the reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 16/84) showing three spots: yellow-green, **17**, R_f 0.65; UV visible, $P(C_6H_{11})_3$, R_f 0.40; dark green, **10**, R_f 0.25. Flash chromatography on silica (eluent, ether/hexane, 7/93) was used to separate the product from the starting materials. A dark green solid, **17**, was obtained (0.1436 g, 0.15 mmol, 58%): mp 62–64 °C; ^{31}P NMR (CD_2Cl_2, 300 K) 52.0 and 50.9 ppm; IR (CH_2Cl_2) ν_{CO} 2090 (w), 2075 (w), 2050 (s), 2025 (s), 2000 (s), 1970 (m), 1930 (m), 1855 (w), 1725 (sh), 1645 (ester) cm^{-1}; FAB mass spectrum: *m*/*z* (relative intensity) 896 (5, $(M - 2CO)^+$), 840 (8, $(M - 4CO)^+$), 784 (71, $(M - 6CO)^+$), 758 (100, $(M - 7CO)^+$, 728 (5, $(M - 5CO - C_6H_{11})^+$), 702 (89, $(M - 6CO - C_6H_{11})^+$), 676 (27, $(M - 7CO - C_6H_{11})^+$), 648 (38, $(M - 5CO - 2C_6H_{11})^+$). Anal. Calcd for $C_{42}H_{57}O_9Co_2MoP$: C, 53.06; H, 6.04. Found: C, 52.94; H, 6.28.

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Synthesis and Chemistry of Thiagermiranes

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Dimethylgermylene (**1**) reacts with thioketones **3** and **9** to give 1,3,2,4-dithiadigermolanes **4** and **10**, the ultimate products of formation of thiagermiranes **6** and **11** and subsequent addition of dimethylgermanethione (**7**). Dimesitylgermylene (**16**) reacts with adamantanethione (**3**) to give 3-(2-adamantyl)-2,2-dimesityl-1,2-thiagermirane (**18**). Photolysis of thiagermirane **18** yields dimesitylgermylene (**16**) and adamantanethione (**3**) derived from germathiocarbonyl ylide **22**. Oxidation of thiagermirane **18** by mCPBA gives 3-(2-adamantyl)-4,4-dimesityl-1,2,4-oxathiagermetane *S*-oxide (**27**). X-ray analyses were done for thiagermirane **18** and 1,2,4-oxathiagermetane *S*-oxide **27**.

Introduction

A great deal of attention both experimental and theoretical has been devoted to cyclic compounds containing metal and hetero atoms, most particularly cyclopropane and cyclobutane systems and their derivatives.[2-7] Since the introduction of strained rings into a molecular environment can have a profound efect on the chemistry of the

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[1] (a) The University of Tsukuba. (b) Sankyo Co., Ltd.

[2] (a) Gordon, M. S.; George, C. *J. Am. Chem. Soc.* **1984**, *106*, 609. (b) Grev, R. S.; Schaefer, H. F. *J. Am. Chem. Soc.* **1987**, *109*, 6577.

[3] (a) Baudler, M.; Jongebloed, H. *Z. Anorg. Allg. Chem.* **1979**, *458*, 9. (b) Hluchy, J.; Klingebiel, U. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 301. (c) Ando, W.; Hamada, Y.; Sekiguchi, A.; Ueno, K. *Tetrahedron Lett.* **1982**, *23*, 5323. (d) Ando, W.; Hamada, Y.; Sekiguchi, A.; Ueno, K. *Tetrahedron Lett.* **1983**, *24*, 4033. (e) Michalczyk, M. J.; West, R.; Michl, J. *J. Chem. Soc., Chem. Commun.* **1984**, 1525. (f) West, R.; De Young, D. J.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 4942. (g) Yokelson, H. B.; Millevolte, A. J.; Gillette, G. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 6865.

0276-7333/89/2308-0161$01.50/0