of $(PhCAs)Co_2(CO)_6$ and 0.84 g (2.2 mmol) of tetraphenylcyclopentadienone in 20 mL of benzene. The solution was freeze-thaw degassed, and the tube was sealed under vacuum. The tube then was placed in an oven at 200 °C for 10 h. At the end of 10 h, the tube was removed from the oven and allowed to cool to room temperature. It was noted that the tube was coated with a shiny metallic mirror. The tube was opened, the contents were filtered, and the tube and the residue were washed with benzene until the washings were clear. The filtrate was reduced in volume and chromatographed on a silicic acid column using benzene as eluent. Benzene eluted a red-purple band which yielded 0.6 g (74% recovery) of tetraphenylcyclopentadienone. Several other bands were noted on the column, but none were in sufficient quantity to isolate.

The shiny black coating which had formed on the walls of the tube was shown to be nonmagnetic and therefore was not cobalt metal. The substance was then tested for arsenic by the method reported in "Comprehensive Analytical Chemistry" for the determination of arsenic by conversion to arsenic trichloride, distilling the arsenic trichloride, and precipitating it as As_2S_3.[30] Following the literature procedure, 0.387 g of the material was shown to contain 0.127 g (33% by weight) of arsenic. This roughly corresponds to the composition Co_2As (38% As by weight) assuming the remainder of the residue was entirely cobalt. The total yield of the black substance was 0.4 g. Therefore, if the composition were indeed Co_2As, 0.4 g represents 2.07 mmol, or a 94% yield of cobalt and arsenic.

Acknowledgment. We are grateful to the National Science Foundation for financial support and to M. K. Gallagher for ^{31}P NMR spectra.

Registry No. 7, R = Me, 69138-19-8; **7**, R = Ph, 69138-20-1; **7**, R = Me_3Si, 69138-21-2; **8**, R = Ph, 68417-27-6; **8**, R = H, 81476-20-2; **8**, R = Me, 68417-26-5; **8**, R = Me_3Si, 81476-21-3; **10**, R = Me, M = W, 69138-17-6; **10**, R = Ph, M = W, 81496-88-0; **10**, R = Me, M = Cr, 69138-16-5; **10**, R = Ph, M = Mo, 81476-22-4; **10**, R = Ph, M = Cr, 81476-23-5; **11a**, 69138-18-7; **11b**, 68417-28-7; $(MeCP)Co_2(CO)_5(PPh_3)$, 81476-24-6; $(MeCP)Co_2(CO)_4(PPh_3)_2$, 81476-25-7; $[(MeCP)Co_2(CO)_5]_3$, 81476-26-8; $(p\text{-}CH_3COC_6H_4CAs)Co_2(CO)_4(PPh_3)_2$, 81476-27-9; $(p\text{-}CH_3COC_6H_4CP)Co_2(CO)_4(PPh_3)_2$, 81476-28-0; $(MeCA_5)Co_2(CO)_4(PPh_3)_2$, 81476-29-1; $(HCAs)Co_2(CO)_4(PPh_3)_2$, 81476-30-4; $(MeCAs)Co_2(CO)_5(PPh_3)$, 81476-31-5; $(PhCAs)Co_2(CO)_4(PPh_3)_2$, 81476-32-6; $(Me_3SiCl)Co_2(CO)_4(PPh_3)_2$, 81476-33-7; $(PhCp)Co_2(CO)_4(PPh_3)_2$, 81476-34-8; $Co_2(CO)_8$, 10210-68-1; $W(CO)_5$, 14040-11-0; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $Cr(CO)_5(THF)$, 15038-41-2; $PhC(O)OCH_3$, 93-58-3; $PhC(O)C(O)OCH_3$, 15206-55-0; Co_2As, 12254-83-0; As_2S_5, 1303-34-0; CH_3CCl_2H, 1300-21-6; PCl_3, 7719-12-2; acetyl chloride, 75-36-5.

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(30) Morries, P. In "Comprehensive Analytical Chemistry"; Wilson, C. L., Wilson, D. W. Eds.; Elsevier: New York, 1962; Vol. Ic, p 237.

(31) Notes added in proof (May 14, 1982). (a) Since this paper was written, the reaction of a stable phosphaacetylene, $(CH_3)_3CC{\equiv}P$, with dicobalt octacarbonyl to give the complex $[(CH_3)_3CCP]CO_2(CO)_6$ has been reported: Burkett-St. Laurent, J. C. T. R.; Hitchcock, P. T.; Kroto, H. W.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1141. (b) An X-ray crystallographic study which has not yet been completed has confirmed the structure of $[PhCPW(CO)_2]CO_2(CO)_6$ ($CPCo_2$ core cluster with $P{-}W(CO)_5$ coordination): Fackler, J. P., Jr., private communication.

Communications

Synthesis of Diastereoisomeric Transition-Metal Complexes with Five Different and Independent Ligands. Resolution through an Optically Active Germanium

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Summary: Optically active germyl ligands are easily introduced in transition-metal complexes. Reaction of optically active $MePh(1\text{-}C_{10}H_7)GeLi$ with $(\eta^5\text{-}C_5H_5)M(CO)_2NO$ (M = Mo, W) results in replacement of CO and formation of anionic species which can be alkylated with CH_3I to afford mixtures of diastereoisomeric complexes, $[(\eta^5\text{-}C_5H_5)M(CO)(NO)(GeR_3)CH_3]$ (R_3 = $MePh(1\text{-}C_{10}H_7)$, M = Mo, W).

Optically active transition-metal complexes in which the metal is chiral are of current interest[1,2] and a few have been obtained with a square-pyramidal geometry. However, up to the present, all complexes of this type obtained have two identical ligands; this is the result of one of the constraints applied to such systems in order to restrict the number of the possible isomers.[2]

In previous work we have described the synthesis of square-pyramidal complexes having five different and independent ligands and have provided evidence for their configurational stability.[3] These complexes can be prepared as a result of the ease of replacement of carbonyl ligands by R_3Ge^- in transition-metal complexes.[4,5]

We report here the synthesis, characterization, and resolution of diastereoisomeric complexes which have a square-pyramidal geometry by means of an optically active germanium substituent. The preparation of the complex (eq 1, M = Mo, W) involves nucleophilic displacement of a carbonyl ligand and methylation of the anion obtained.

Slow addition of 10 mmol of (methylphenyl-1-naphthylgermyl)lithium[6] (prepared by stirring at room temperature for 1 h 2.92 g (10 mmol) of $MePh(1\text{-}C_{10}H_7)GeH$ ($[\alpha]^{25}_D$ ± 26°) and 10 mmol of *n*-butyllithium in 20 mL of ether) to a solution of 2.5 g (10 mmol) of $(\eta^5\text{-}C_5H_5)Mo(CO)_2NO$[7] in 50 mL of ether at room temperature resulted in smooth evolution of carbon monoxide as the

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[1] Brunner, H.; Mokhlesur Rahman, A. F. M. *J. Organomet. Chem.* **1981**, *214*, 373 and preceding papers.

[2] Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 251 and references therein.

[3] Colomer, E.; Corriu, R. J. P.; Vioux, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 476.

[4] Colomer, E.; Corriu, R. J. P. *J. Chem. Soc., Chem. Commun.* **1978**, 435.

[5] Carré, F.; Cerveau, G.; Colomer, E.; Corriu, R. J. P. *J. Organomet. Chem.*, in press.

[6] Brook, A. G.; Peddle, G. J. D. *J. Am. Chem. Soc.* **1963**, *85*, 2338.

[7] Hoyano, J. K.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1978**, *10*, 126.

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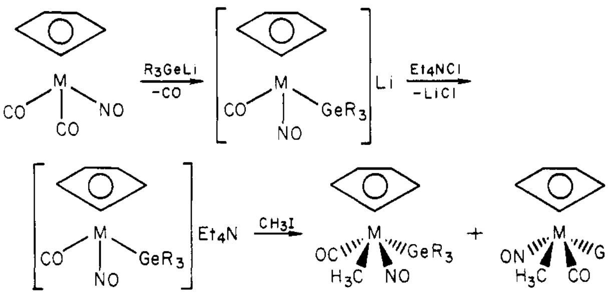
orange color of the complex turned brown.[8] After the solution was stirred at room temperature for 5 h, the solvent was pumped off and the residue taken up in 50 mL of CH_2Cl_2; then 2 g of Et_4NCl dissolved in 10 mL of CH_2Cl_2 was added at room temperature. The solution was filtered through a fritted funnel (G4), the solvent pumped off, and the residue taken up in THF. After filtration, THF was pumped off and the residue dissolved in CH_2Cl_2. Slow addition of hexane formed two layers, and the mixture was left at −20 °C. After 3–4 days a brown gum precipitated; this gum was freed from the solvent and dissolved in THF. To this solution was added 2 mL of CH_3I at room temperature; a precipitate of Et_4NI appeared and the brown solution turned orange-yellow. The solvent was pumped off and the residue dissolved in toluene and filtered. The solution was concentrated and chromatographed on silica gel using toluene/hexane (1/1) as eluant. A yellow band was collected and the solvent removed to leave an orange-yellow solid residue (1.30 g, yield 25%). The ^1H NMR[9] spectrum of the product corresponds to a mixture of two diastereoisomers, which have the CO and NO ligands trans each to other as deduced from the IR spectrum (ν(CO) 2010, ν(NO) 1650 cm^{-1} in CH_2Cl_2[10,11]). Fractionnal crystalization from toluene/hexane (for the less soluble diastereoisomer) and from hexane (for the more soluble diastereoisomer) allowed the separation of both complexes.[12,13]

The configurations at molybdenum are unknown. However, the configuration at germanium should be the same as in the starting germane, since optically active germyllithium is known to react always with retention of configuration in its reactions either with organic substrates[6,14] or with transition-metal complexes.[5]

The same procedure with (η^5-C_5H_5)W(CO)$_2$NO[7] led to the formation of a mixture of diastereoisomers where M = W (eq 1)[15,16] which are separated as above.[17]



(1)

M = Mo, W R_3 = MePh(1-$C_{10}H_7$)

The ORD curves for the (+) and (−) diastereoisomers (for M = Mo, W), which differ only in the transition-metal configuration, are almost mirror images of each other, because the ORD is mainly determined by the metal chromophore and the chirality in the ligands makes only minor contributions. This observation has been reported previously.[2,18]

These complexes do not epimerize in solution at 25 °C for 24 h. However, at 60 °C a slow decomposition occurs, and in 1 h the optical rotation is only the half of that of the starting material. UV irradiation leads to fast decomposition.

This work is of particular significance for two reasons: (i) this is the first example of the resolution of diastereoisomeric complexes of a transition metal, in which the latter is chiral, having five different and independent ligands, and (ii) we report here the use of an optically active metalloid (germanium) to resolve optically active complexes of a metal (molybdenum or tungsten). The advantage of this method, compared to the resolution by means of phosphines, consists of the fact that the formation of the Ge–metal bond is not reversible and avoids any epimerization through a reversible process.

Registry No. (η^5-C_5H_5)Mo(CO)(NO)(GeR$_3$)CH$_3$ isomer 1, 81521-58-6; (η^5-C_5H_5)Mo(CO)(NO)(GeR$_3$)CH$_3$ isomer 2, 81496-99-3; (η^5-C_5H_5)W(CO)(NO)(GeR$_3$)CH$_3$ isomer 1, 81521-57-5; (η^5-C_5H_5)W(CO)(NO)(GeR$_3$)CH$_3$ isomer 2, 81496-98-2; (η^5-C_5H_5)Mo(CO)$_2$NO, 12128-13-1; (η^5-C_5H_5)W(CO)$_2$NO, 12128-14-2; (*S*)-(−)-MePh(1-$C_{10}H_7$)GeH, 22430-39-3; (*R*)-(+)-MePh(1-$C_{10}H_7$)GeH, 23190-27-4; MePh(1-$C_{10}H_7$)GeLi isomer 1, 41839-37-6; MePh(1-$C_{10}H_7$)GeLi isomer 2, 41839-66-1.

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(8) All experiments were carried out under nitrogen by using dried and deaerated solvents.

(9) ^1H NMR (δ relative to Me_4Si in C_6D_6) 7–8.3 (m, aromatic), 4.70 (s, C_5H_5), 1.33 (s) and 1.37 (s) (CH_3Ge), 0.78 (s) and 0.80 (s) (CH_3Mo).

(10) Addition of (triphenylgermyl)lithium to (η^5-C_5H_5)Mo(CO)$_2$NO at −78 °C and further methylation at room temperature affords a mixture of the three isomers.[3] However, when the addition of germyllithium is carried out at room temperature, only the trans isomer is obtained after alkylation.

(11) For optically inactive complexes the trans isomer has IR absorptions at ~2010 cm^{-1}, while the cis isomers absorb ~1925 cm^{-1}. Cf. ref 3.

(12) Starting with (*S*)-(−)-MePh(1-$C_{10}H_7$)GeH less soluble complex: mp 115–116 °C dec; $[\alpha]^{25}_D$ −130°, $[\alpha]^{25}_{578}$ −140°, $[\alpha]^{25}_{546}$ −184°, $[\alpha]^{25}_{436}$ −483° (benzene); ^1H NMR signals at δ 1.33 and 0.78. More soluble complex: mp 78–80 °C dec; $[\alpha]^{25}_D$ +123°, $[\alpha]^{25}_{578}$ +134°, $[\alpha]^{25}_{546}$ +179°, $[\alpha]^{25}_{436}$ +381° (benzene).

(13) All new complexes gave satisfactory elemental analyses (±0.4%).

(14) Eaborn, C.; Hill, R. E. E.; Simpson, P. *J. Organomet. Chem.* **1968**, *15*, P1; **1972**, *37*, 267 and 275. Carré, F.; Corriu, R. *J. Organomet. Chem.* **1974**, *65*, 349.

(15) From 10 mmol of germyllithium and 10 mmol of (η^5-C_5H_5)W(CO)$_2$NO (3.34 g) were obtained 3.1 g of the mixture of diastereoisomers (yield 51%).

(16) ^1H NMR (δ relative to Me_4Si in C_6D_6) 6.8–8.5 (m, aromatic), 4.66 (s, C_5H_5), 1.38 (s) and 1.42 (s) (CH_3Ge), 0.82 (s) and 0.85 (s) (CH_3W); IR (CH_2Cl_2) for both diastereoisomers ν(CO) 2010, ν(NO) 1635 cm^{-1}.

(17) Starting with (*R*)-(+)-MePh(1-$C_{10}H_7$)GeH less soluble complex: mp 140–141 °C; $[\alpha]^{25}_D$ +164°, $[\alpha]^{25}_{578}$ +176°, $[\alpha]^{25}_{546}$ + 228°, $[\alpha]^{25}_{436}$ +422°; ^1H NMR signals at δ 1.38 and 0.82. More soluble complex: mp 118–120 °C; $[\alpha]^{25}_D$ −144°, $[\alpha]^{25}_{578}$ −155°, $[\alpha]^{25}_{546}$ −211°, $[\alpha]^{25}_{436}$ −239°.

(18) Brunner, H. *Angew. Chem., Int. Ed. Engl.* 1971, *10*, 249.

Stereochemistry of Nucleophilic Cleavage of Silicon (or Germanium)–Transition Metal Bonds. The Case of Octahedral Complexes: an Exception to the Leaving Group Rule

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Summary: Nucleophilic cleavage of hexacoordinated complexes of Mn, Re, and W always takes place with low retention of configuration (stereoselectivity from 55 to 70%). Such retention is observed whatever the nature of the ligands. Whether they are in the cis or trans position to the silyl or germyl group in the octahedral structure has no effect.

The factors which control nucleophilic substitution at silicon are now well-known.[1,2] These reactions generally

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(1) Sommer, L. H. "Stereochemistry, Mechanism and Silicon" McGraw-Hill, New-York 1965.