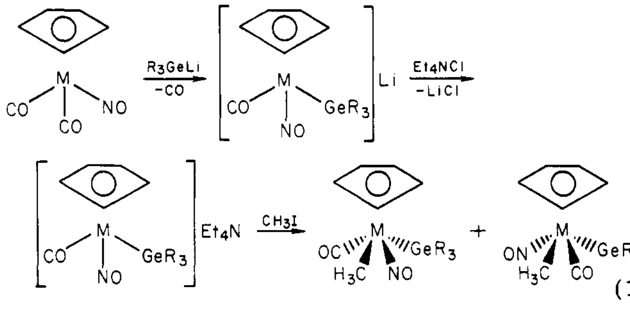
orange color of the complex turned brown.[8] After the solution was stirred at room temperature for 5 h, the solvent was pumped off and the residue taken up in 50 mL of CH_2Cl_2; then 2 g of Et_4NCl dissolved in 10 mL of CH_2Cl_2 was added at room temperature. The solution was filtered through a fritted 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 ^{1}H 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] ^{1}H 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); ^{1}H 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] ^{1}H 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°; ^{1}H 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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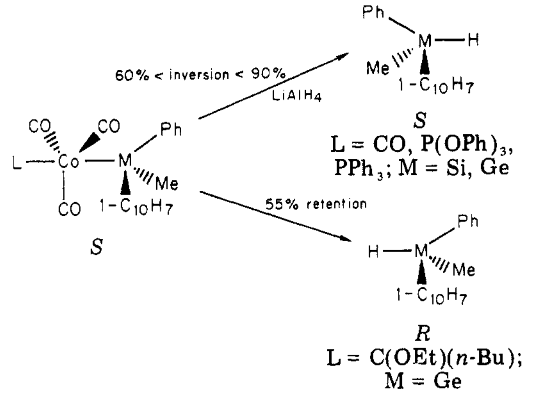
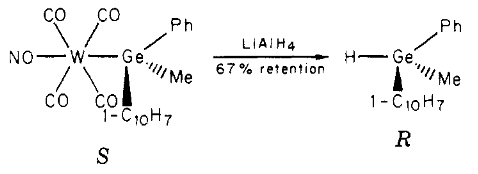
[1] Sommer, L. H. "Stereochemistry, Mechanism and Silicon" McGraw-Hill, New-York 1965.

Scheme I



Scheme II



are stereoselective: a R_3Si-X (R_3 = MePh(1-$C_{10}H_7$)) bond is substituted either with predominant retention or with predominant inversion of configuration at silicon depending on several factors, in particular: (i) the nature of the leaving group X and (ii) the electronic character of the nucleophilic reagent. The same factors are important for optically active compounds of germanium.[3]

We have tried to extend these rules to the case of silicon (or germanium)-transition metal bonds. We observed previously that the cleavage of a silicon (or germanium)-transition metal bond by $LiAlH_4$ proceeds by nucleophilic attack at silicon (or germanium).[4] Such compounds are good examples for these stereochemical studies because it is very easy to change the nature of the leaving group by means of the electronic character of the ligands at the transition metal.

The results obtained in the cleavage by $LiAlH_4$ of cobalt complexes of the type $(CO)_3LCoMR_3$ (L = CO and PR_3 for M = Si and Ge and L = C(OEt)(n-Bu) for M = Ge)[5,6] are in good agreement with the general rules on nucleophilic displacement at silicon:[7] they vary from predominant inversion to predominant retention of configuration, depending on the nature of the ligands (Scheme I). $(CO)_4Co$ is a poor nucleophile[8] and thus it behaves as a good leaving group: 90% inversion is observed. Substitution of one carbonyl by electron-donating ligands decreases the ability of the transition metal to be substituted,[9] in the order CO > $P(OPh)_3$ > PPh_3 > C(OEt)R, and the percentage of inversion decreases in the same order (Scheme I).[6] Furthermore, changes in stereochemistry were observed by changing the nature of the nucleophile.[10]

Scheme III

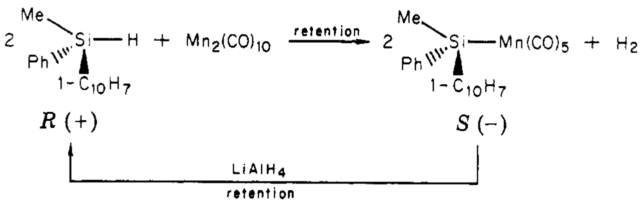


Table I. Cleavage Reactions with $LiAlH_4$ in Et_2O[16]

compd	$[\alpha]^{25}_D$ (pentane), deg	stereochemistry,[a] %
$(CO)_5MnSiR_3$	-107	71 RN
$PPh_3(CO)_4MnSiR_3$	-150	66 RN
$(CO)_5MnGeR_3$	-60.5	57 RN
$(CO)_4[C(OEt)Me]MnGeR_3$	-369	57 RN
$(CO)_4[C(OEt)Me]MnGeR_3$	-369	62 RN[b]
$(CO)_4[C(OEt)Me]ReGeR_3$	-239	53 RN
$(CO)_4NOWGeR_3$[6]	-85	67 RN

[a] RN = retention. [b] Solvent = dimethoxyethane. Maximum rotations: MePh(1-$C_{10}H_7$)SiH $[\alpha]^{25}_D$ ±36° and MePh(1-$C_{10}H_7$)GeH $[\alpha]^{25}_D$ ±26.7° (cyclohexane). The percentages of stereochemistry are calculated as defined in ref 15, assuming that all complexes are optically pure.

Table II. Comparative Stereochemistries for Nucleophilic Cleavages with Different Reagents[a]

nucleophile	stereochemistry % for $(CO)_5MnSiR_3$	 % for R_3SiF
$LiAlH_4$ (suspension in Et_2O)	71 RN	
$LiAlH_4$ (suspension in DME)	69 RN	
$LiAlH_4$ (solution in Et_2O)	68 RN	95 INV[17]
$LiAlH_4$/LiBr (solution in Et_2O)	67 RN	62 RN[17]
ROH	57 RN[b]	
ROH/RONa	53 RN[c]	80 INV,[d,18] 57 INV[f,18] 94 RN,[e,18] 100 RN[g,18]
H_2O	66 RN	

[a] DME = dimethoxyethane; RN = retention; INV = inversion. [b] R = Me. [c] R = Me, MeOH (mol)/MeONa (mol) = 4.3. [d] R = n-Bu, n-BuOH (mol)/n-BuONa (mol) = 38. [e] R = n-Bu, n-BuOH (mol)/n-BuONa (mol) = 1.5. [f] R = i-Pr, i-PrOH (mol)/i-PrONa (mol) = 66. [g] R = i-Pr, i-PrOH (mol)/i-PrONa (mol) = 4.3. Cleavage reactions with water, methanol, and methanol/methoxide, respectively, led to silanol and methoxysilane which are reduced to the respective silane with full retention of configuration.[19] The stereochemistries were determined as described previously with Walden cycles.[15]

Nevertheless, we have recently noticed one exception. The complex $(CO)_4(NO)WGeR_3$, in spite of its electronic similarity with $(CO)_4CoMR_3$, was cleaved with predominant retention of configuration instead of the expected inversion (Scheme II).[6] In order to understand better the nature of the silicon (or germanium)-transition metal bond, we have investigated other complexes in which the transition metal is surrounded by the same type of ligands. Thus, we synthesized two sets of complexes, $(CO)_4LM-M'R_3$ (where L = CO, PPh_3, M = Mn, M' = Si, and L = CO, C(OEt)Me, M = Mn, Re, M' = Ge),[11] and we studied

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[2] Corriu, R. J. P. *J. Organomet. Chem. Libr.* **1980**, *9*, 357. Corriu, R. J. P.; Guérin, C. *J. Organomet. Chem.* **1980**, *198*, 231 and references therein.

[3] Eaborn, C.; Hill, R. E. E.; Simpson, P. *J. Organomet. Chem.* **1972**, *37*, 251. Brook, A. G.; Peddle, G. J. D. *J. Am. Chem. Soc.* **1963**, *85*, 2338. Carré, F.; Corriu, R. *J. Organomet. Chem.* **1974**, *65*, 343.

[4] Colomer, E.; Corriu, R. J. P.; Vioux, A. *J. Chem. Res., Synop.* **1977**, 168; *J. Chem. Res., Miniprint* **1977**, 1939.

[5] Colomer, E.; Corriu, R. J. P. *J. Chem. Soc., Chem. Commun.* **1976**, 176; *J. Organomet. Chem.* **1977**, *133*, 159.

[6] Cerveau, G.; Colomer, E.; Corriu, R. J. P. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 478.

[7] Sommer, L. H.; Frye, C. L.; Musolf, M. C.; Parker, G. A.; Rodewald, P. G.; Michael, K. W.; Okaya, Y.; Pepinsky, R. *J. Am. Chem. Soc.* **1961**, *83*, 2210.

[8] King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417.

[9] Curtis, M. D. *Inorg. Chem.* **1972**, *11*, 802.

[10] Cerveau, G.; Colomer, E.; Corriu, R. J. P., unpublished results.

their cleavage by different nucleophiles. The stereochemistries were determined through Walden cycles as shown in Scheme III.

We confirmed that the cleavage takes place by nucleophilic attack at silicon since reaction of $(CO)_5MnSiPh_3$ with $LiAlD_4$ gave only Ph_3SiD. The results obtained for the cleavage reaction with $LiAlH_4$ are reported in Table I. The stereochemistry observed was always predominant retention of configuration whatever the nature of the ligands and the structure of the complex (cis or trans).

We cleaved the optically active complex $(CO)_5MnSiMePh(1\text{-}C_{10}H_7)$ with different nucleophiles. Our results are reported in Table II. The stereochemistry is always predominant retention of configuration. This is the first case in which the stereochemistry of nucleophilic displacement at silicon is quite independent of the electronic features of both leaving group and attacking nucleophile. For complexes such as $(CO)_5MnSiR_3$, the leaving group $(CO)_5Mn$, like $(CO)_4Co$, is a poor nucleophile.[8] It should be a good leaving group, and inversion of configuration is the normally expected stereochemistry.[1,2] The replacement of a CO ligand by electron-donating ligands does not change the stereochemistry of the cleavage reaction in contrast to the cobalt–silicon cleavage.[6]

When the electronic character of the nucleophilic reagent was changed, no change in stereochemistry was observed. In particular, we have selected two known examples: (i) the use of $LiAlH_4/LiBr$, instead of $LiAlH_4$, which causes a change in the stereochemistry from predominant inversion to retention of configuration for some fluorosilanes[17] (Table II) and (ii) the addition of MeONa to MeOH, which displaces the stereochemistry from predominant inversion to retention[18] (Table II). Such effects are not observed in the case of the manganese complexes. In all cases a low retention of configuration was obtained. The main difference between cobalt and manganese (or rhenium or tungsten) compounds is their geometry: cobalt complexes are trigonal bipyramidal; the others are octahedral. We believe that this first reported exception to the leaving group rule, observed for octahedral complexes, is certainly connected with their geometry.

Further work is in progress in order to determine whether or not the mechanism is actually the same in the two cases.

Registry No. (*S*)-(–)-$(CO)_5MnSiMePh(1\text{-}C_{10}H_7)$, 81476-81-5; (*R*)-(+)-$(CO)_5MnGeMePh(1\text{-}C_{10}H_7)$, 81476-82-6; *trans*-(*S*)-(–)-$PPh_3(CO)_4MnSiMePh(1\text{-}C_{10}H_7)$, 81476-83-7; *cis*-(*S*)-(–)-$(CO)_4$-$[ClOEt)Me]MnGeMePh(1\text{-}C_{10}H_7)$, 81476-84-8; *cis*-(*S*)-(–)-$(CO)_4[C(OEt)Me]ReGeMePh(1\text{-}C_{10}H_7)$, 81476-85-9; (*R*)-(+)-$MePh(1\text{-}C_{10}H_7)SiH$, 1025-08-7; (*S*)-(–)-$MePh(1\text{-}C_{10}H_7)GeH$, 22430-39-3; $Mn_2(CO)_{10}$, 10170-69-1.

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(11) $(CO)_5MnM'R_3$ (M′ = Si, Ge) were prepared by thermal reaction at 150° between $(CO)_{10}Mn_2$ and optically active $MePh(1\text{-}C_{10}H_7)M'H$ according to: Jetz, W.; Simons, P. B.; Thompson, J. A. G.; Graham, W. A. G. *Inorg. Chem.* **1966**, *5*, 2217. These compounds were oils, and their optical purity is therefore unknown. Starting with (*R*)-(+)-$MePh(1\text{-}C_{10}H_7)SiH$,[12] we obtained (*S*)-(–)-$(CO)_5MnSiMePh(1\text{-}C_{10}H_7)$ $[\alpha]^{25}{}_D$ –107° (pentane), and with (*S*)-(–)-$MePh(1\text{-}C_{10}H_7)GeH$,[13] we obtained (*R*)-(+)-$(CO)_5MnGeMePh(1\text{-}C_{10}H_7)$ $[\alpha]^{25}{}_D$ +60.5° (pentane). We assume in our calculations that these maximum rotations correspond to the optically pure compounds. *trans*-(*S*)-(–)-$PPh_3(CO)_4MnSiR_3$, $[\alpha]^{25}{}_D$ –150°, was obtained as orange crystals, mp 201–203 °C, from (*R*)-(+)-R_3SiH, according to: Schrieke, R. R.; West, B. O. *Aust. J. Chem.* **1969**, *22*, 49. *cis*-(*S*)-(–)-$(CO)_4[C(OEt)Me]MGeR_3$ (M = Mn, Re) was prepared as in ref 14. All complexes have the same absolute configuration as the starting materials for the same reasons invoked in ref 5 and 6. New complexes gave satisfactory elemental analyses (±0.4 %).

(12) Corriu, R. J. P.; Moreau, J. J. E. *Bull. Soc. Chim. Fr.* **1975**, 901.

(13) Brook, A. G.; Peddle, G. J. D. *J. Am. Chem. Soc.* **1963**, *85*, 1869.

(14) Carré, F.; Cerveau, G.; Colomer, E.; Corriu, R. J. P. *J. Organomet. Chem.*, in press.

(15) Sommer, L. H.; Citron, J. D.; Parker, G. A. *J. Am. Chem. Soc.* **1969**, *91*, 4729.

(16) Cleavage reactions were performed as in ref 4.

(17) Corriu, R. J. P.; Fernandez, J. M.; Guérin, C. *Tetrahedron Lett.* **1978**, 3391.

(18) Sommer, L. H.; Fujimoto, H. *J. Am. Chem. Soc.* **1969**, *91*, 7040.

(19) Reference 1, p 73.

Carbon Monoxide Insertion into a Uranium–Carbon Double Bond. The Structure of $(\eta^5\text{-}C_5H_5)_3U(\eta^2\text{-}OCCH)P(CH_3)(C_6H_5)_2$

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Summary: The complex $(\eta^5\text{-}C_5H_5)_3U(\eta^2\text{-}OCCH)P(CH_3)(C_6H_5)_2$ crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell of dimensions a = 16.54 (2) Å, b = 10.31 (1) Å, c = 17.372 (9) Å, β = 117.60 (6)°, V = 2962 (4) Å^3, and ρ_{calcd} = 1.51 g/cm^3. The structure has been refined by the least-squares method to the final error indices on F of R_1 = 0.053 and R_2 = 0.063 with 112 variables and 1536 data. The three η^5-cyclopentadienyl ligands and a η^2-β-ketoylide coordinate tetrahedrally about the uranium(IV) ion. Within the η^2-CO unit, the U–O distance 2.27 (1) Å is shorter than the U–C distance 2.37 (2) Å.

We have recently prepared and determined the structure of $(\eta^5\text{-}C_5H_5)_3U{=}CHPR_3$ (1),[1] in which the uranium–carbon bond can be ascribed multiple bond character.[2] Since the availability of 1 presents an opportunity to examine the behavior of the heretofore unknown uranium carbon double bond, we have begun to investigate the chemistry of 1. We report here a facile CO insertion into this bond.

Solutions of 1 in toluene react with CO under atmospheric pressure. At ambient temperature, green toluene solutions of 1 become red within 0.5 h. After concentration and addition of heptane, red crystalline 2 precipitates at –15 °C. Spectroscopic and chemical analysis indicate the formulation shown in eq 1.[3] NMR demonstrates that the Cp_3U and $CHPR_3$ groups retain their integrity and molecular weight measurements show **2a** to be monomeric in benzene solution. Since these data do not determine the details of the carbon monoxide binding, a single-crystal

$$\begin{aligned} 1 + \mathrm{CO(1\ atm)} \xrightarrow[25\ ^\circ\mathrm{C}]{\text{toluene}} & (\eta^5\text{-}C_5H_5)_3U(\eta^2\text{-}OCCH)PR_1R_2R_3 \\ & \mathbf{2a},\ R_1 = CH_3,\ R_2 = R_3 = C_6H_5 \\ & \mathbf{2b},\ R_1 = R_2 = CH_3,\ R_3 = C_6H_5 \end{aligned} \qquad (1)$$

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(1) Cramer, R. E.; Maynard, R. B.; Gilje, J. W. *Inorg. Chem.* **1981**, *20*, 2466–2470.

(2) Cramer, R. E.; Paw, J. C.; Maynard, R. B.; Gilje, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 3589–3590.

(3) 2a: NMR (^{1}H in C_6D_6, chemical shifts relative to internal C_6H_6, positive shifts downfield) +53.64 (1 H, d, J_{HCP} = 35 Hz), –0.40 (4 H, dd, J_{HCP} = 12 Hz, J_{HCCH} = 7 Hz), –1.09 (2 H, t, J_{HCCH} = 7 Hz, –1.51 (4 H, t, J_{HCCH} = 7 Hz), –6.88 (3 H, d, J_{HCP} = 14 Hz), –18.61 ppm (15 H, s). Anal. Calcd for $UPOC_{30}H_{29}$: C, 53.41; H, 4.34; P, 4.59; mol wt 675. Found: C, 55.65; H, 4.45; P, 4.60; mol wt 719 (cryoscopic in benzene). 2b: NMR (^{1}H in C_6D_6, chemical shifts relative to internal C_6H_6, positive shifts downfield) +56.30 (1 H, d, J_{HCP} = 36 Hz), –0.80 (2 H, dd, J_{HCP} = 12 Hz, J_{HCCH} = 7 Hz), –1.31 (1 H, t, J_{HCCH} = 7 Hz), –1.85 (2 H, t, J_{HCCH} = 7 Hz), –6.07 (6 H, d, J_{HCP} = 14 Hz), –18.58 ppm (15 H, s). Anal. Calcd for $UPOC_{25}H_{27}$: C, 49.02; H, 4.45; P, 5.06. Found: C, 48.09; H, 4.47; P, 5.05.

0276-7333/82/2301-0869$01.25/0