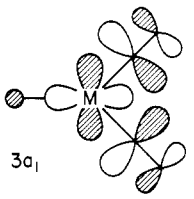
orbitals at the lower left are essentially the W–CO σ bonds, in and out of phase combinations of carbonyl lone pairs with appropriate W hybrids. The $2a_1$ and $1b_1$ orbitals are formally assigned to the metal, though "back-bonding" with carbonyl π^* obviously occurs for these.

Above these orbitals is a substantial energy gap and a group of other metal- and ligand-based levels. Important in the subsequent discussion is the $3a_1$ orbital, **2**. This level is localized mainly on the carbonyls, with an antibonding admixture of metal d.

2

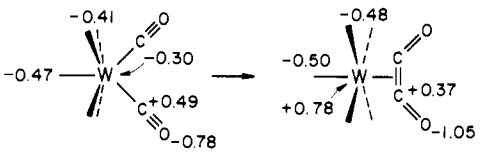


For a d^4 electron count on the seven-coordinate uncoupled side the reaction is nicely allowed. The coupled side is disfavored by 0.9 eV, primarily as a consequence of destabilization of $1b_2$ along the reaction coordinate. Thus the C–C bond formation process in d^4 seven-coordinate carbonyl or isocyanide complexes is a symmetry-allowed reaction, but it emerges in our calculations as an energetically uphill process. How might it be promoted? Two strategies are suggested, focusing respectively on (i) direct reduction and (ii) charge evolution along the reaction coordinate.

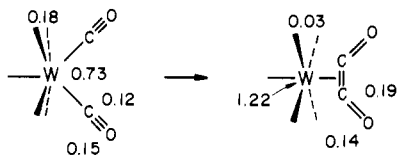
If two electrons were added to the d^4 seven-coordinate complex, they would perforce enter a high-lying orbital. This is not surprising, given that one is beginning with an 18-electron complex. But just a little motion along the reaction coordinate would find the electrons in an orbital that is descending rapidly in energy. The orbital in question is $3a_1$, which is M–C antibonding and C–C bonding and so moves to lower energy as the carbonyl carbons approach either. It would be stabilized further if two protons or other Lewis acids were attached to the electronegative X group bound to carbon in the terminal stages of the coupling, forming a bound acetylene ligand.

The strategy suggested by this is clearly reduction, preferably beginning with a geometry in which the carbonyls or isocyanides have already come part way together. This π-acid ligand proximity is common in seven-coordinate complexes, where C–M–C angles near 70° are observed.[2,5] In general acute angles are promoted by higher coordinate compounds with linear ligands.

Pursuing another line of thought, we show in **3** how the net



3 net charges



4 electron densities in $1b_2$

charges in a d^4 complex evolve along the reaction coordinate and in **4** the distribution of the two electrons in the $1b_2$ orbital, the one rising in energy along the reaction coordinate. The electron-density changes are in principle the basis for a synthetic stretegy: σ and π acceptors, or more electronegative groups, are to be placed where the electron density accumulates, at the sites that grow more negative. Ligands that are σ and π donors, or electropositive groups, facilitate the reaction if put in the sites that grow positive. The problem is obvious—the total electron-density variation is opposite to that of the $1b_2$ orbital-density change. Model calculations in which the ligand or metal electronegativities or donor properties are changed confirm this difficulty. They further indicate that the total charge density effects "win out", but not by much. The effect of the five ligands is small although a better σ or π acceptor as the girdle ligand helps a little. A more electropositive metal definitely lowers the barrier to coupling. This is in accord with the concept of oxidizing the metal while reductively coupling the C≡X ligands. Looking at the system with two electrons more ($3a_1$ occupied), one obtains similar conclusions. Results similar to the above are obtained when isocyanides are considered instead of carbonyls. In support of our strategy is the fact that reductive coupling of $[Mo(CNR)_6X]^+$ complexes best occurs when the redox potential of the Mo(II) → Mo(III) couple is least positive.[6]

We look forward to experimental realization of this new reaction type.

Acknowledgment. We thank John Ellis for bringing some relevant work to our attention. Support by the National Science Foundation of the work at Cornell (CHE 7828048) and at Columbia (CHE 8109390) is gratefully acknowledged, as is support by the donors of Petroleum Research Fund, administered by the American Chemical Society, at North Carolina.

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Palladium-Catalyzed Stereocontrolled Cyclization of 1,3-Diene Monoepoxides and Its Application to the Synthesis of 11-Deoxy-PGE_1

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Palladium(0)-catalyzed allylic alkylation is a useful synthetic method.[1] The stereoselectivity of this reaction in acyclic systems, however, has not been studied as much as the regioselectivity in both cyclic and acyclic systems.[2] In this communication we report the regio- and stereoselective formation of δ-lactones **5** and **10** by intramolecular nucleophilic displacement of 1,3-diene monoepoxides[3] **1** and **8**, respectively, catalyzed by palladium complexes (Scheme I). If the 1,3-diene monoepoxide moiety serves to control the 1,4 relative stereochemistry between the newly formed carbon bond and the allylic alcohol and also the geometry of the resulting olefin, this overall transformation would be valuable for the synthesis of prostaglandins (PGs). Since one of the major problems in previous syntheses of PGs was the stereoselective generation of the relative stereochemistry between C(15) and C(12), including the geometry of the Δ^{13}-olefin. Regiospecific introduction of an α-side chain to **5** and the conversion of the

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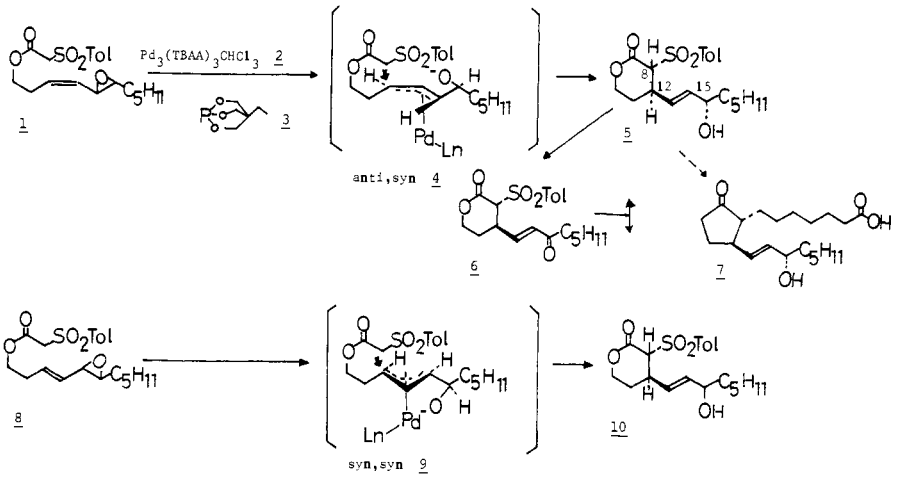
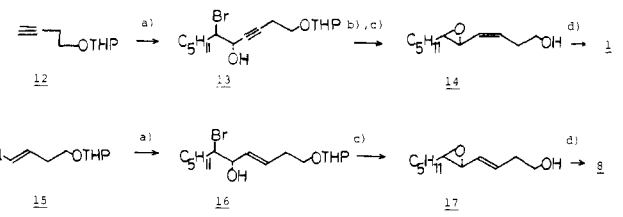
Scheme I



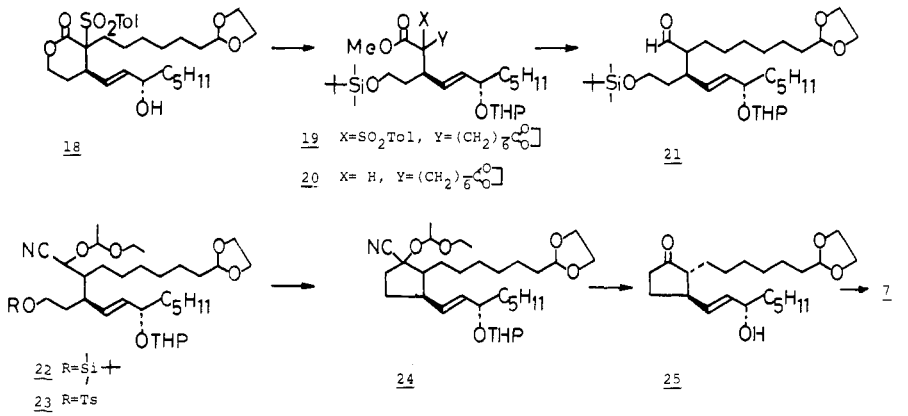
Scheme II



[a] *n*-BuLi, at −78 °C, 96%. [b] 5% Pd/$BaSO_4$ in MeOH/quinoline. [c] Camphorsulfonic acid/MeOH, 30% aqueous KOH; overall yield 93% from 13 or 16. [d] *p*-tolSO_2CH_2COOH/$EtO_2CN{=}NCO_2Et$/PPh_3; 85% (**1**), 80% (**8**). [e] The stereoselectivity was higher than 95%.[5]

phosphite ligand **3** in THF at room temperature without base for 4–5 h. The cyclized products were obtained in 60–70% yields. The cyclization of **1** gave a mixture of the δ-lactones **5** and **10** in a ratio of 92:8, while the reaction of **8** led to a mixture of the δ-lactones **5** and **10** in a ratio of 5:95. No regioisomer (the eight-membered lactone) was detected in either case by careful examination (NMR, HPLC).[8] The trans stereochemistry between C(8) and C(12) (PG numbering) and the *E* configuration of the resulting olefins, in both **5** and **10**, were established by NMR spectra.[8] The lactones **5** and **10** were diastereoisomers, epimeric at C(15), which was confirmed by the transformation of the lactone **5** to the enone **6** [Me_2SO $(COCl)_2$ in CH_2Cl_2 and then Et_3N], followed by nonstereoselective reduction (L-Selectride in THF at −78 °C) to give a mixture of **5** and **10**. The relative

Scheme III



δ-lactone to the cyclopentanone by applying the protected cyanohydrin method[4] should give the 11-deoxy PGE_1 (**7**). On the basis of the above methodology, we examined the stereoselectivity of the cyclization of (*E*)-5,6-epoxy-(*Z*)-3-undecen-1-yl (*p*-tolylsulfonyl)acetate (**1**) and its olefinic isomer **8**, respectively.

The esters **1** and **8** were prepared stereoselectivity by starting from 2-bromoheptanal (**11**) as outlined in Scheme II.

Cyclization of the ester **1**[6] and **8**[6] was carried out by using 1–2 mol % of palladium(0) catalyst **2**[7] and 12–24 mol % of the stereochemistry between C(12) and C(15), in both **5** and **10**, however, was not clear by NMR analyses. The lactone **5** was converted to 11-deoxy PGE_1 (**7**) (Scheme III) in order to confirm the relative stereochemistry. These results and mechanistic consideration based on previous work[2] indicate that the cycliization of **1** and **8** proceeds with overall retention of the stereochemistry of the epoxide through palladium complexes **4** and **9**, respectively. In this transformation, the initial ionization of monoepoxides occurs with inversion of configuration, and the following cyclization also

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(6) Ester **1**: NMR (90 MHz, $CDCl_3$) δ 2.43 (s, 3 H, $PhCH_3$), 2.68–2.96 (m, 1 H, epoxide proton), 3.26 (dd, *J* = 2, 8 Hz, 1 H, epoxide proton), 5.18 (dd, *J* = 8, 11 Hz, 1 H, olefinic), 5.58 (dt, *J* = 8, 11 Hz, 1 H, olefinic); high-resolution mass spectrum, calcd for $C_{20}H_{28}O_5S$ *m/e* 380.1657, found *m/e* 380.1678. Ester **8**: 2.48 (s, 3 H, $PhCH_3$), 2.73–2.92 (m, 1 H, epoxide proton), 3.08 (dd, *J* = 2, 8 Hz, 1 H, epoxide proton), 5.33 (dd, *J* = 8, 16 Hz, 1 H, olefinic), 5.83 (dt, *J* = 7, 16 Hz, 1 H, olefinic); high-resolution mass spectrum, calcd for $C_{20}H_{28}O_5S$ *m/e* 380.1657, found *m/e* 380.1640.

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(8) Lactone **5**: NMR (90 MHz, $CDCl_3$) δ 4.00 (d, *J* = 5 Hz, $CHSO_2$), 5.64 (dd, *J* = 2.5, 16 Hz, olefinic), 5.73 (dd, *J* = 3, 16 Hz, olefinic); IR 1730 cm^{-1}; HPLC retention time 9.0–10.0 min (silica gel 60–5 μm, 7.5 o.d. × 250 mm, 5.2 mL/min, 5% isopropyl alcohol in hexane); high-resolution mass spectrum, calcd for $C_{20}H_{28}O_5S$ *m/e* = 380.1657, found *m/e* 380.1660. Lactone **10**: NMR δ 4.00 (d, *J* = 5 Hz, $CHSO_2$), δ 5.66 (dd, *J* = 1.5, 16 Hz, olefinic), 5.73 (dd, *J* = 3, 16 Hz, olefinic); IR 1730 cm^{-1}; HPLC retention time 12.5–13.5 min; high-resolution mass spectrum, calcd for $C_{20}H_{28}O_5S$ *m/e* = 380.1657, found *m/e* 380.1656.

proceeds without isomerization of the anti,syn complex **4** to syn,syn form **9**.

The transformation of **5** into 11-deoxy-PGE_1 (**7**) was carried out in the following way. Alkylation of the tetrahydropyranyl ether of **5** with 1-iodo-7,7-(1,3-dioxolane)heptane (NaH in DMF at 50 °C for 4 h) gave the alkylated product **18** in 45% yield. The lactone **18** was converted into the ester **19** in three steps (KOH in MeOH, CH_2N_2, and *t*-$BuMe_2SiCl$/imidazole) and the desulfonylation of **19** [5% Na(Hg) Na_2HPO_4 in EtOH at room temperature for 12 h] gave the ester **20** in 93% yield. Conversion of the ester **20** to the aldehyde **21** (*i*-Bu_2AlH in THF at −50 °C, $Me_2SO/(COCl)_2$ and then Et_3N, overall yield 86%), cyanohydrin formation (Me_3SiCN/KCN−18-crown-6 at 0 °C, $PhCH_2NMe_3F$ in THF/H_2O at 0 °C for 30 min), and the protection of the cyanohydrin [CH_2=CHOEt/pyridinium *p*-toluenesulfonate (PPTS) in CH_2Cl_2] gave **22** in 95% overall yield. Removal of the silyl group (*n*-Bu_4NF in THF at room temperature for 3 h) and the tosylation of the resulting alcohol ($TsCl/Et_3N$ in CH_2Cl_2) gave **23** in 89% overall yield. Cyclization of the protected cyanohydrin **23** was carried out[4] in 95% yield in refluxing THF with sodium bis(trimethylsilyl)amide. Removal of the hydroxy protecting groups in **24** (PPTS in MeOH at 40 °C for 3 h), followed by base treatment (K_2CO_3 in MeOH at room temperature for 30 min), gave **25** in 90% overall yield. Hydrolysis of the acetal (0.1 N HCl in acetone), reprotection of the allyl alcohol (CH_2=CHOEt/PPTS in CH_2Cl_2), followed by oxidation of the aldehyde ($AgNO_3$/aqueous KOH in EtOH at room temperature for 5 h), and removal of the ethoxyethyl group (0.1 N HCl in acetone) gave 11-deoxy-PGE_1 (**7**). Esterification of **7** with diazomethane gave the methyl ester of 11-deoxy PGE_1, which was identical in all respects (NMR, TLC, HPLC) with an authentic sample.[9]

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Registry No. (±)-**1**, 83918-40-5; **2**, 5436-04-4; **3**, 824-11-3; (±)-**5**, 83918-41-6; (±)-**5** (THP ether), 83918-42-7; (±)-**6**, 83918-43-8; (±)-**7**, 34603-80-0; (±)-**7** (methyl ester), 34603-79-7; (±)-**8**, 83918-44-9; (±)-**10**, 83946-23-0; (±)-**11**, 83918-45-0; **12**, 40365-61-5; (±)-**13**, 83918-46-1; (±)-**14**, 83918-47-2; **15**, 83918-48-3; (±)-**16**, 83918-49-4; (±)-**17**, 83946-24-1; **18**, 83918-50-7; **19**, 83918-51-8; **20**, 83928-39-6; **21**, 83928-40-9; **21** (cyanolhydrin), 83928-41-0; **22**, 83928-42-1; **23** (R = H), 83928-43-2; **23**, 83928-44-3; **24**, 83918-52-9; **24** (diol), 83918-53-0; (±)-**25**, 83918-54-1; **25** (protected aldehyde), 83918-55-2; (±)-*erythro*-6-bromo-5-hydroxy-1-[(tetrahydropyran-2-yl)oxyl]undec-3(*Z*)-ene, 83946-25-2.

(9) We are indebted to Ono Pharmaceutical Co. for providing an authentic sample of **7**.

Transition-Metal Insertion into Naked Metal Cluster Polyanions

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Received August 2, 1982

Recently, considerable interest has developed in the study of naked metal clusters. Species that have been known for decades in solution such as Sn_9^{4-} and Sb_7^{3-} have been isolated in the solid state and characterized.[1] The nature of these species in solution has also been studied,[2] and they appear to be fluxional. Many new species have been synthesized, for example, Sn_4^{2-}, Sn_5^{2-}, Pb_5^{2-}, Sn_8Tl^{5-}, $Sn_{9-x}Ge_x^{4-}$, (x = 0–9), Sn_xPb_{9-x} (x = 0–9), $Tl_2Te_2^{2-}$, Ge_9^{4-}, and others.[1-9] Despite this activity, however, no metal cluster containing a transition metal in addition to a main-group metal has yet been reported. The extreme sensitivity of these polyanions toward oxygen together with the difficulty of isolating pure homogeneous species from solution has greatly hindered progress toward this objective. However, ^{119}Sn and ^{207}Pb NMR spectroscopy has proven to be a sensitive and reliable investigative tool for species in solution. With this technique, for the first time clear evidence of the existence of compounds that contain a transition metal bonded to a naked metal cluster moiety has been obtained.

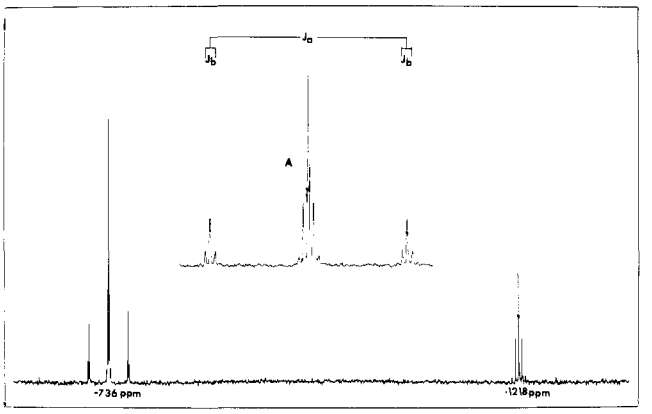

Figure 1. ^{119}Sn NMR spectrum of the mixture $K_4[Sn_9]$ and $K_4[(PPh_3)_2PtSn_9]$. Spectrum A was achieved by using a smaller widow: $J_a \equiv J_{^{195}Pt-^{119}Sn}$, $J_b \equiv J_{^{119}Sn-^{117}Sn}$. Chemical shifts are referenced to tetramethyltin.

Earlier attempts to obtain naked cluster species such as $Sn_xM_z^{q-}$, where M is a transition metal, by extracting alloys of composition $K_ySn_xM_z$ with ethylenediamine (en) have been unsuccessful.[10] This result is not surprising since metal clusters have many points of similarity with boron hydrides,[11] and in boron chemistry, compounds involving a naked transition metal are not known. However, metal–ligand moieties are very common in metalloborane and metalloheteroborane chemistry.

Addition of the zerovalent platinum complex, $Pt(PPh_3)_4$, to a solution of $K_4[Pb_9]$ in en, in an equimolar ratio, causes a slow but gradual change in color of the solution from dark red-brown to green brown. The solution was investigated at both 18.7 and 74.8 MHz by ^{207}Pb NMR. The ^{207}Pb NMR spectra displayed only a triplet at 27.1 ppm and a singlet at 1154.1 ppm, upfield from 1 M $Pb(NO_3)_2$.[12] The singlet was assigned to Pb_9^{4-} by comparison with an authentic sample of this anion in en. The frequency separation between the two outermost peaks of the triplet is independent of the applied field and this, together with the relative areas of the triplet (1:4:1), leads us to propose that this compound is a lead cluster containing a platinum atom of the form $Pb_xPtL_y^{q-}$ ($J_{^{195}Pt-^{207}Pb}$ = 4122 Hz). Because of the fluxionality of this species in solution no indication of the value of x is possible from ^{207}Pb NMR.

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[‡] Deceased May 11, 1981.

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(8) Cisar, A.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 632–635.
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(11) See, for instance: Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1–66.
(12) Due to the fluxional nature of Pb_9^{4-} in solution, all chemical environments are equivalent.

0002-7863/83/1505-0149$01.50/0