Table I. Kinetic Data[a] for Reaction 1 in Cyclohexane

T, °C	$10^5 k_{obsd}$, s^{-1}			
50.0	4.76[b]	4.90[c]	4.83[d]	4.85[e]
50.2	5.05	5.19[f]	5.22[g]	
61.6	15.9	16.2	17.2	
70.0	40.0	42.2	39.9	

[a] $\Delta H^\ddagger = 22.22 \pm 0.44$[h] kcal mol^{-1}, $\Delta S^\ddagger = -9.6 \pm 1.3$ cal K^{-1} mol^{-1}, $\sigma(k_{obsd}) = \pm 5.0\%$.[i] 10^4[complex] = 2.2–4.4 M; 10^4[dppm] = 5.6 M unless otherwise indicated. [b–e] 10^4[dppm] = 0, 14.5, 28.9, and 30.1 M, respectively. [f] Solution equilibrated with 40% CO–N_2 gas mixture. [g] Solution equilibrated with pure CO. [h] Uncertainties are estimates of standard deviations adjusted for the number of degrees of freedom so that 95% confidence limits can be obtained by doubling them. [i] Standard deviation of an individual measurement of k_{obsd}.

It was identified spectroscopically in situ and after isolation.[9] $Os_3(CO)_{10}(\mu\text{-dppm})$ was prepared by the very rapid reaction of $Os_3(CO)_{10}(NCMe)_2$[8] with dppm and characterized spectroscopically[10] and by analysis.[12] It is identical with the product of reaction 1 and the mode of preparation confirms the bridging nature of the dppm ligand.

The progress of reaction 1 is accompanied by a slight increase in intensity of the electronic absorption band at ca. 350 nm and a decrease of absorbance of the maximum at 417 nm, the latter shifting to 410 nm.[14] Isosbestic points are evident at 392 and 330 nm. Rate constants were obtained graphically from the absorbance changes at 410 nm and are shown in Table I together with the activation parameters. The rate constants are not sensitive to the presence of O_2 and are independent of [complex], [dppm], and [CO]. Free dppm had no effect on the nature of the product so no competing intermolecular substitution of an additional dppm ligand occurred. The absence of any retardation by CO shows that simple reversible CO dissociation is not rate determining, nor does it precede the rate-determining step.

Since the data in Table I are the first of their type there are no activation parameters for direct comparison and even studies involving intramolecular chelate ring formation have seldom involved determination of temperature dependence of the rates. An exception to this is the extensive study of the reaction shown in eq 2.[3c] When M = Cr and LL = dppm the values of $\Delta H^\ddagger$ and

$$M(CO)_5(\eta^1\text{-LL}) \rightarrow M(CO)_4(\eta^2\text{-LL}) + CO \qquad (2)$$

$\Delta S^\ddagger$ are 33.7 kcal mol^{-1} and +17.0 cal K^{-1} mol^{-1}, respectively. The high value of $\Delta H^\ddagger$ and the positive value of $\Delta S^\ddagger$ both indicate a high degree of Cr–CO bond breaking in the transition state, the values being very close to those for dissociation of CO from $Cr(CO)_5(PPh_3)$, viz., $\Delta H^\ddagger = 35.3$ kcal mol^{-1} and $\Delta S^\ddagger = +14.4$ cal K^{-1} mol^{-1}.[15] This shows that bond making is negligible or small and that the mechanism of chelate ring closure is essentially I_d in nature.

The activation parameters in Table I lead to quite the opposite conclusion for the bridge-formation reaction shown in eq 1. The much lower value of $\Delta H^\ddagger$ and the substantially negative value of $\Delta S^\ddagger$ both point strongly to an associative mechanism. This conclusion is supported by the activation parameters for the [P-*n*-Bu$_3$]-independent introduction of P-*n*-Bu$_3$ into $Os_3(CO)_{11}$(P-*n*-Bu$_3$) which are $\Delta H^\ddagger = 39.6 \pm 1.0$ kcal mol^{-1} and $\Delta S^\ddagger = +24 \pm 3$ cal K^{-1} mol^{-1} whereas those for the corresponding associative substitution are 15 ± 1 kcal mol^{-1} and -36 ± 3 cal K^{-1} mol^{-1}, respectively.[11] While it would be preferable to have data for reaction of $Os_3(CO)_{11}(PPh_2Me)$ with PPh_2Me it is unlikely that they would be substantially different. The activation parameters show, therefore, that the bridge formation reaction involves a high degree of bond making and can be unambiguously classified as I_a or S_N2 in nature.

The difference between the values $\Delta S^\ddagger = -36$ cal K^{-1} mol^{-1} for the intermolecular associative attack of P-*n*-Bu$_3$ on $Os_3(CO)_{11}$(P-*n*-Bu$_3$) and $\Delta S^\ddagger = -9.6$ cal K^{-1} mol^{-1} for bridge formation must reflect, to a large degree, the much higher effective concentration of the uncoordinated P atom in $Os_3(CO)_{11}(\eta^1\text{-dppm})$. The difference amounts to a factor of ca. 5×10^5 in rates. This is somewhat lower than the factor of ca. 10^8 generally expected but it is by no means unusual.[17] This aspect of such reactions can now be investigated further by studying the dependence of the kinetic parameters on the nature of various bridging ligands such as $R_2P(CH_2)_nPR_2$.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council, Ottawa, for support.

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(9) ν_{CO} in cyclohexane: 2098 (m), 2048 (ms), 2026 (sh), 2010 (s), 2000 (sh), 1988 (w), 1980 (w), 1967 (w), 1953 (w) cm^{-1}. Cf. $Os_3(CO)_{11}(PPh_3)$, ν_{CO}: 2108 (ms), 2055 (s), 2035 (s), 2009 (s), 2000 (ms), 1989 (ms), 1978 (m) cm^{-1}.[8] Traces of $Os_3(CO)_{10}(\mu\text{-dppm})$ were evident[10] in the isolated complex and consequently no elemental analysis was attempted.

(10) ν_{CO} in cyclohexane: 2088 (s), 2027 (sh), 2006 (vs), 1983 (s), 1965 (m), 1955 (m), 1945 (w) cm^{-1}. Cf. $Os_3(CO)_{10}$(P-*n*-Bu$_3$)$_2$, ν_{CO} in decalin: 2070 (m), 2012 (s), 1995 (s), 1958 (m), 1950 (w), 1935 (w) cm^{-1}.[11]

(11) Poë, A. J.; Sekhar, V. C., unpublished results.

(12) Anal. Calcd for $Os_3(CO)_{10}$(dppm): C, 34.03; H, 1.78. Found:[13] C, 34.69; H, 1.62.

(13) Microanalysis performed by Canadian Microanalytical Service, Ltd., Vancouver.

(14) $Os_3(CO)_{11}(\eta^1\text{-dppm})$ shows maxima in cyclohexane at 410 (ϵ 6.4×10^3 M^{-1} cm^{-1}) and 350 nm (ϵ 1.14×10^4 M^{-1} cm^{-1}); $Os_3(CO)_{10}(\mu\text{-dppm})$ shows maxima at 417 (ϵ, 5.2×10^3 M^{-1} cm^{-1}) and 354 nm (ϵ 1.2×10^4 M^{-1} cm^{-1}).

(15) These parameters are derived from values of E_a and k_{obsd} at 30 °C. Atwood, J. D.; Cohen, M. A.; Brown, T. L. unpublished results quoted in reference 16.

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Chiral Vinyllithium Reagents. Carbenoid Reactions[1]

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The reaction of an organic halide that possesses a proton on the halogen-bearing carbon with a lithium reagent can lead to either halogen–lithium exchange[2,3] or hydrogen–lithium exchange (metalation[4]). The latter reaction results in the formation of intermediates known as carbenoids,[5,6] which are capable of undergoing ambiphilic reactions.[7–9] During the course of our study of chiral vinyllithium reagents,[10] prepared by halogen–lithium exchange, we often observed side products which could be rationalized as resulting from nucleophilic substitution on a vinylidene carbenoid. The stereochemical investigation of this reaction is the subject of this communication.

Treatment of (*aS*)-(+)-(4-methylcyclohexylidene)bromomethane (**1**) of known absolute configuration[10] in ether at −90

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(1) This work was presented at the 187th ACS national meeting held in St. Louis, April 8–13, 1984.

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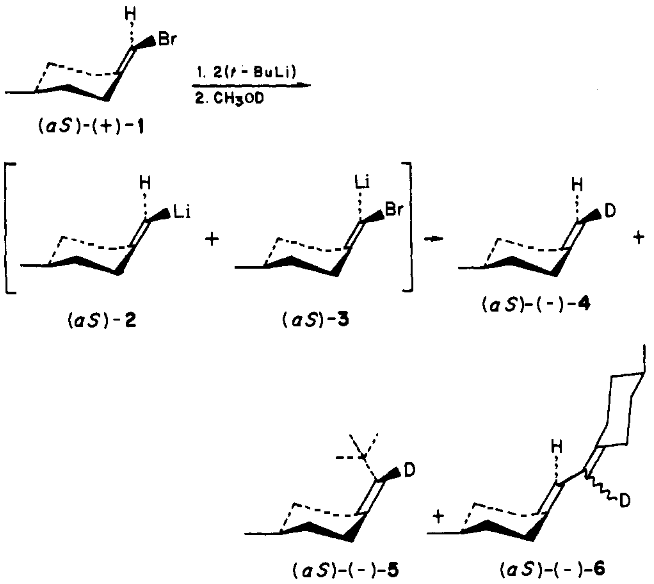
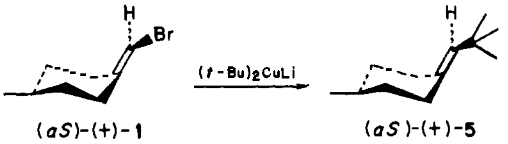
0002-7863/84/1506-5035$01.50/0

°C with 2 equiv of *t*-BuLi[11] followed by deuterolysis yielded (*aS*)-(−)-(4-methylcyclohexylidene)deuteriomethane (**4**), (*aR*)-(−)-1-(4-methylcyclohexylidene)-1-deuterio-2,2-dimethylpropane (**5**), and (*aS*)-(−)-1,2-bis(4-methylcyclohexylidene)-2-deuterioethane (**6**) with 1.0 deuterium in each compound. Compound **4** is the major product, which is the result of the usual halogen-metal exchange, whereas **5** and **6** are products derived from the carbenoid **3**. The formation of **3** and therefore **5** and **6** could be suppressed by carrying out the reaction in THF.



Although Bothner-By and others[9] have previously observed nucleophilic-type substitution on carbenoid species, the stereochemistry of the reaction has yet to be elucidated.[5b,12] Köbrich[13a] has demonstrated that carbenoids similar to **3** are only capable of maintaining configurations at temperatures lower than −85 °C. Hence under our experimental conditions one would have expected **3** to lose its configuration and produce racemic **5**. However, **5** was found to be *optically active and to be of inverted configuration.*



That inversion did occur was established by reacting (*aS*)-(+)-**1** with lithium di-*tert*-butylcuprate to yield (*aS*)-(+)-**5**. Since this reaction is known to proceed with complete retention of configuration,[14] the absolute configuration as well as optical purity for **5** has therefore been determined.

The formation of (*aS*)-(−)-**6**, whose structure, configuration, and optical purity has previously been established,[15] can be explained by the addition of the optically stable vinyllithium **2** to the racemic carbenoid or carbene[9] followed by hydrolysis with methanol-*d*. This would account not only for the retention of configuration but for the ~50% optical purity observed. The ^{13}C NMR spectrum substantiated that **6** was a mixture, in equal amounts, of two diastereomers.

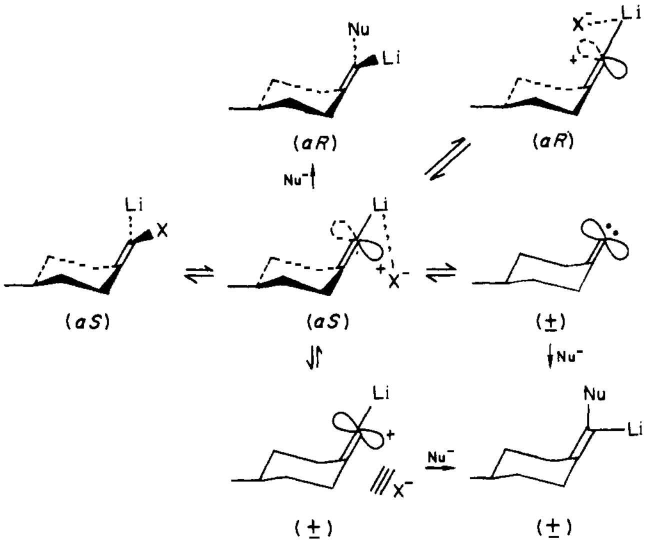
Since vinyl chlorides undergo the metalation reaction at a much faster rate than the chlorine–lithium exchange with *tert*-butyllithium, this would diminish the formation of products such as **4** and **6** and would result largely in the formation of a carbenoid intermediate and produce **5** as the major product. Chiral (*aS*)-(+)-**7**, $[\alpha]^{28}{}_{\mathrm{Hg}}$ 56.93 ± 0.44°, was prepared in 87% yield by treating (*aS*)-**2**, formed in THF at −90 °C, with benzenesulfonyl chloride. At −75 °C treatment of **7** with 2 equiv of *tert*-butyllithium in ether or THF followed by deuterolysis gave (*aR*)-(−)-**5** as the major product and only ~5% of **4**, and no detectable amount of **6** was produced. Again, the result was clear; **5** was produced with overall inversion of configuration. The results are summarized in Table I.

Table I. Reaction of (*aS*)-(+)-(4-Methylcyclohexylidene)methyl Halides with *tert*-Butyllithium

halide	solvent	*T*, °C	**4**, % yield (% OP)	**5**, % yield (% OP)[a]	**6**, % yield (% OP)[b]
Br	Et$_2$O	−90	58 (100)	17 (39 ± 3)	0.5 (58 ± 3)
Br	THF	−90	90 (100)	5 (53 ± 3)	5.0 (50 ± 1)
Cl	Et$_2$O	−75		36 (31 ± 2)	
Cl	THF	−75		70 (39 ± 3)	

[a] Based on optically pure **5**, $[\alpha]^{27}{}_{\mathrm{Hg}}$ 9.68 ± 0.24° (*c* 1.0, CHCl$_3$). [b] Based on optically pure **6**, $[\alpha]^{27}{}_{\mathrm{Hg}}$ 40.3 ± 0.7° (*c* 0.63, absolute EtOH).[15]

Scheme I. Metal-Assisted Ionization



On the basis of available data, we propose the mechanism shown in Scheme I.

It has been suggested,[16] on the basis of ^{13}C NMR data, that carbenoids like **3** are electron deficient at carbon and therefore would be expected to behave as electrophiles. The weakening of the carbon–halogen bond would be consistent with NMR data, and we suggest that this weakening is assisted by the lithium attached to the same carbon atom as the halogen (carbenoid). During the ionization process the carbenoid carbon would undergo rehybridization placing the developing positive charge in a p orbital and producing a tight ion pair.[17] The leaving halide would block one enantioface of the substrate, and the nucelophile, in this case *tert*-butyllithium, would attack from the opposite side leading to inversion of configuration. When the leaving halide becomes solvent separated the substrate is linear and capable of rotating, and configuration is completely lost. Another mode of racemi-

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zation, occurring within the solvent cage, can be visualized. This involves a lithium atom behaving as a pivotal point about which the halogen can migrate from one side to the other. This is also the case when both the lithium and halogen have to produce a carbene. Reaction of *tert*-butyllithium with these species leads to racemic **5**. The net result is overall inversion of configuration. The process is reminiscent of solvolysis reactions involving chiral substrates. Although vinyl halides ionize with extreme difficulty, carbenoids (metal-substituted vinyl halides) appear to ionize more readily. We refer to this as *metal-assisted ionization*. The mechanism can also be applied to the Fritsch–Buttenburg–Wiechell rearrangement in which it has been shown that the migrating group has a trans relationship with the leaving group.[18]

Acknowledgment. We thank the National Science Foundation for financial support of this work.

Registry No. (a*S*)-(+)-**1**, 60164-94-5; (a*S*)-(−)-**4-*d***, 91296-37-6; (a*R*)-(−)-**5-*d***, 91296-38-7; (a*S*)-(+)-**5**, 91296-39-8; (a*S*)-(−)-**6-*d*** (isomer 1), 91383-55-0; *t*-BuLi, 594-19-4; (*t*-Bu)$_2$CuLi, 23402-75-7; (a*S*)-(−)-**6-*d*** (isomer 2), 91296-40-1.

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Synthesis and Characterization of Stable Cobalt(IV) Coordination Complexes: Molecular Structure of *trans*-[η^4-1,2-Bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene]bis(4-*tert*-butylpyridine)cobalt(IV)

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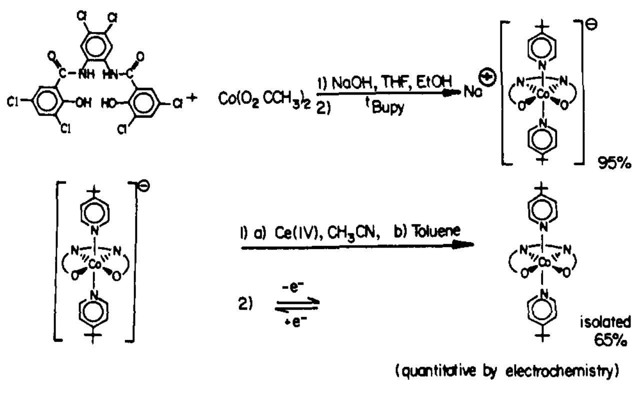
We are interested in contributing to oxidation chemistry by preparing coordination complexes with transition metals in unusual, high oxidation states for use as oxidizing agents. Our approach has been to employ multianionic chelating ligands that have been designed to be compatible with highly oxidized metal centers and the media necessary to generate them.[2] Here we report the synthesis of stable complexes of Co(IV) and their characterization by spectroscopic and single-crystal X-ray diffraction methods. With the exception of several homoleptic halide and oxide complexes,[3] this work contains the first structural study of a Co(IV) coordination complex.[4] The oxidative electrochemistry of a number of cobalt coordination compounds has been previously investigated.[5] Organocobalt(IV) complexes have been detected by cyclic voltammetry.[6] In addition, several of these complexes have been generated at low temperature and characterized by EPR spectroscopy.[7]

Scheme I



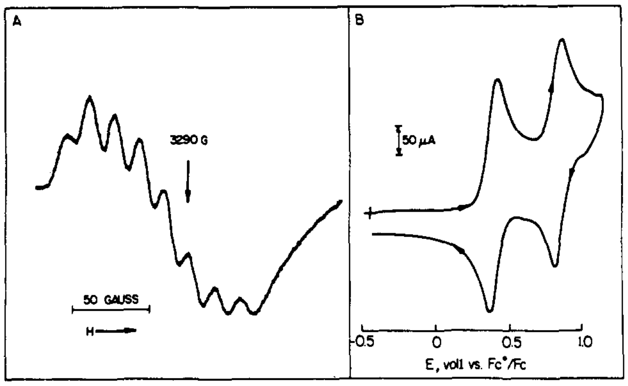


Figure 1. A: First derivative EPR spectrum of *trans*-Co(η^4-CHBA-DCB)(*t*-Bupy)$_2$ in frozen toluene at 10 K. Microwave frequency is 9.198 MHz. B: Cyclic voltammogram of 3.7 mM Na[*trans*-Co(η^4-CHBA-DCB)(*t*-Bupy)$_2$]·H$_2$O in CH$_3$CN, 0.1 M TBAP at 0.174-cm^2 BPG electrode. Scan rate = 200 mV/s^{-1}.[11]

Treatment of Co(O$_2$CCH$_3$)$_2$ with 1 equiv of H$_4$(CHBA-DCB)[2,8] in THF/EtOH followed by addition of excess NaOH and 4-*tert*-butylpyridine (*t*-Bupy) yields a deep red solution after stirring for 0.5 h at room temperature (Scheme I). The complex Na[*trans*-Co(η^4-CHBA-DCB)(*t*-Bupy)$_2$]·H$_2$O was isolated in 95% yield by removal of excess *t*-Bupy under vacuum and filtration through silica gel in THF. The solid obtained by evaporation of the THF solution was recrystallized from CH$_2$Cl$_2$/hexane.[9] Oxidation of Na[*trans*-Co(η^4-CHBA-DCB)(*t*-Bupy)$_2$]·H$_2$O with 1 equiv of ceric ammonium nitrate in CH$_3$CN affords *trans*-Co(η^4-CHBA-DCB)(*t*-Bupy)$_2$ in 65% isolated yield by removal of CH$_3$CN under vacuum and extraction into, and crystallization from, toluene.[10]

The dark green complex was characterized by its EPR spectrum in frozen toluene solution at 10 K (Figure 1A), which shows the eight-line pattern expected for a Co ($I = {}^7/_2$) centered radical at $g = 2.011$ with Co hyperfine splitting of 1.5×10^{-3} cm^{-1} (16 G). The g value is similar to and the isotropic hyperfine coupling slightly larger than those reported for organobis(dioximato)co-

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(8) Abbreviations: H$_4$(CHBA-DCB), 1,2-bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene; H$_4$(CHBA-Et), 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane; *t*-Bupy, 4-*tert*-butylpyridine; py, pyridine; THF, tetrahydrofuran; Et, ethyl; SCE, saturated calomel electrode; BPG, basal plane pyrolytic graphite; TBAP, tetrabutylammonium perchlorate; DMAP, 4-dimethylaminopyridine; Fc, ferrocene.

(9) ^{1}H NMR spectroscopic data: ((CD$_3$)$_2$CO) δ 9.38 (s 2 H), 8.22 (d, J = 6 Hz, 4 H), 7.83 (d, J = 3 Hz, 2 H), 7.22 (d, J = 6 Hz, 4 H), 7.13 (d, J = 3 Hz, 2 H), 3.04 (s, (H$_2$O, 2 H), 1.16 (s, 18 H). Anal. Calcd for C$_{38}$H$_{34}$Cl$_6$CoN$_4$NaO$_5$: C, 49.54; H, 3.72; N, 6.08. Found: C, 49.28; H, 3.78; N, 6.16.

(10) Anal. Calcd for C$_{38}$H$_{32}$Cl$_6$CoN$_4$O$_4$: C, 51.84; H, 3.66; N, 6.36. Found: C, 51.51; H, 3.83; N, 6.08.