ands that have been studied by Taube and co-workers.[1] Since these reactions are charge symmetric, it is usually tacitly assumed that $\Delta S^\circ \approx 0$ and hence $\Delta S_{FC}^* \approx 0$.[1b,3b,c] However, since reaction entropies for high-spin Co(III)/Co(II) couples are generally found to be markedly larger than for Ru(III)/Ru(II) and other low-spin couples (Table I),[10,13] large positive values of ΔS° and hence ΔS_{FC}^* are therefore anticipated for these reactions.

As an illustrative example, we consider the intramolecular reduction of Co(III) by Ru(II) in $(H_2O)Ru(NH_3)_4(bpy)Co(NH_3)_5^{5+}$ (where bpy = 4,4′-bipyridine). The reaction for the corresponding decaammine complex $Ru(NH_3)_5(bpy)Co(NH_3)_5^{5+}$ is liable to involve a net entropy change of ca. 20–25 eu since the reaction entropies of Co(III)/Co(II) and Ru(III)/Ru(II) couples having similar ligands uniformly differ by this amount (Table I).[10,14] The effect of replacing one ammonia on ruthenium by an aquo ligand can be gauged from the 7 eu larger reaction entropy for $Ru(NH_3)_5OH_2^{3+/2+}$ than for $Ru(NH_3)_6^{3+/2+}$ (Table I). (To a first approximation, the reaction entropies for mixed-ligand complexes appear to arise from linear additive contributions from each ligand.[13]) Thus, the entropic driving force for electron transfer in $(H_2O)Ru^{II}(NH_3)_4(bpy)\text{-}Co^{III}(NH_3)_5^{5+}$ is estimated to be ca. +15 eu. Bearing in mind the likely value of ΔS_{int}^* (1–2 eu[9]), a value of ΔS_{FC}^* of ca. 8 eu is obtained from eq 3a. Therefore, the "measured" activation entropy, ΔS_a^*, of 2.5 eu for this system is suggestive of a significantly nonadiabatic pathway ($\kappa_{el} \sim 0.1$ (eq 1)] rather than the adiabatic pathway that has been inferred without consideration of the entropic driving force.[1b,c] Since similar values of ΔS_{FC}^* should also be appropriate for other $(H_2O)Ru^{II}(NH_3)_4LCo^{III}(NH_3)_5^{5+}$ reactions with related bridging ligands L, the smaller or negative values of ΔS_a^* seen, for instance, with L = 1,2-bis(4-pyridyl)ethylene (1.3 eu) and 1,2-bis(4-pyridyl)ethane (−9.6 eu)[3b,c] infer the presence of decidedly nonadiabatic pathways. Thus, from eq 1, if $\Delta S_{FC}^* = 8$ eu, then κ_{el} is $\sim 3 \times 10^{-2}$ and $\sim 1 \times 10^{-4}$ for these two reactions, respectively.

Naturally, these resulting κ_{el} values should be regarded as being only approximate. Since the values of ΔS_{rc}° for the intramolecular binuclear reactions are inferred from data for structurally similar mononuclear couples, the reliability of the resulting estimates of ΔS° and hence ΔS_{FC}^* may be called into question. Unfortunately, values of ΔS° cannot be measured directly for these and other thermal intramolecular reactions on account of the rapid aquation that follows the formation of Co(II). However, Steggerda et al. have shown that the values of ΔS_{rc}° for mononuclear Ru(III)/Ru(II) couples containing pyrazine ligands are essentially the same as in binuclear complexes where the pyrazine ligand is also bound to another ruthenium redox center.[30] This result therefore provides strong support to the present method for estimating ΔS° values for binuclear complexes. Providing that the present estimates of ΔS° are accurate to within ca. 5 eu, which seems reasonable, then the corresponding estimates of κ_{el} are reliable within ca. 4-fold.

Such entropic driving-force effects also provide a rationalization of the substantially more positive value of ΔS_a^*, 10.4 eu, for electron transfer in $(SO_3)Ru^{II}(NH_3)_4(pyr)Co^{III}(NH_3)_5^{3+}$,[1d] especially in comparison with that for $(H_2O)Ru^{II}(NH_3)_4(bpy)Co^{III}(NH_3)_5^{5+}$, 2.6 eu. This increase is difficult to explain on the basis of electronic coupling effects[1d] but can easily be understood in terms of the influence of nonbridging ligand composition on ΔS° and hence ΔS_{FC}^*. The presence of anionic ligands generally yields substantially smaller values of ΔS_{rc}°.[10,13] The influence of substituting an aquo for a sulfite ligand on the reaction entropy of Ru(III)/Ru(II) can be gauged roughly from the decrease in ΔS_{rc}° 15 eu, between $Ru(NH_3)_5OH_2^{3+/2+}$ and *cis*-$Ru(NH_3)_4Cl_2^{+/0}$ (Table I),[10] corresponding to an increase in ΔS_{FC}^* of ca. 8 eu (Eq 3a) since the ruthenium undergoes oxidation.

Similar considerations can also be applied to a number of other intramolecular reactions, such as those involving nonsymmetrical bridging ligands.[1d,32] We have also recently analyzed activation parameter data for a number of intramolecular redox reactions at metal surfaces (i.e. electrochemical processes involving adsorbed reactants) in a similar manner.[33] Entropic driving-force effects are generally important for these processes since only one redox center is involved, so that ΔS° equals ΔS_{rc}°. The estimation of ΔS_{FC}^* for intramolecular systems should be approached with caution since the factors influencing the thermodynamic entropy changes are incompletely understood. Nevertheless, it is clear that careful consideration of the ligand composition and the chemical as well as electrostatic nature of the redox centers is required in order to evaluate the contribution of the Franck–Condon entropy to the measured preexponential factors.

Acknowledgments. We are grateful to Drs. J. E. J. Schmitz and J. J. Steggerda for supplying details of their reaction entropy measurements on binuclear complexes prior to publication. Helpful synthetic expertise was provided by Dr. Tomi Li. This work is supported by the Air Force Office of Scientific Research.

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Unexpected Formation of *cis*- and *trans*-$Ph_2PCH{=}CHPPh_2$ by Reaction of Lithiobis(diphenylphosphino)methane and Dichloromethane. ^{13}C NMR Studies of the Products

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Lithiobis(diphenylphosphino)methane (**1**) shows an ambivalent reactivity toward organo halides.[1,2] The carbanionic center as well as the two trivalent phosphorus atoms may be attacked alternatively by the electrophiles RX. Reactions of **1** with methyl iodide or benzyl chloride proceed according to (1) while diphenylchlorophosphine affords products of type **3**. If instead of **1** the methylated derivative $[Li(TMED)]^+[Ph_2PCHPPhMe]^-$ (TMED = tetramethylethylenediamine) is used, dialkylchlorophosphines R'_2PCl (R′ = $t\text{-}C_4H_9$, C_6H_{11}) attack at the more basic phosphorus atom, forming products of type **3**, $Ph_2PCH{=}PPhMePR'_2$.[2]

Looking for synthetic routes to new polydentate phosphine ligands with P–C–P units, we studied the reaction between **1**

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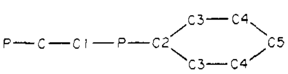
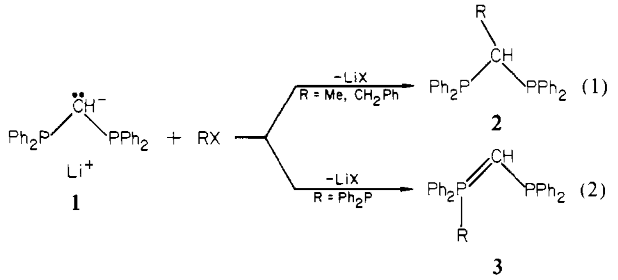
Table I. $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR Data of the Compounds **1**, **8**, and **9**[f]

	$^{31}P^a$	$^{13}C\{^1H\}^b$										
	δ_P	δ_{C1}	J_{AC1}	J_{BC1}	δ_{C2}	J_{AC2}	δ_{C3}	J_{AC3}	δ_{C4}	J_{AC4}	δ_{C5}	$^3J_{PP}$
1[c]	−3.6											
8a (cis)	−23.1	146.0	15.6[d]		138.5	−8.4	132.7	20.1	128.2	6.5	128.3	100[e]
8b (trans)	−8.4	142.1	−19.0	21.0	137.0	−10.1	133.2	19.6	127.8	6.6	128.3	13.6
9a (cis)		137.7	76.6	−17.0	130.4	86.1	126.3	12.9	129.3	10.8	130.0	21.4
9b (trans)		140.3	70.8	2.5	129.8	87.0	126.8	12.7	129.2	10.8	129.9	58.5

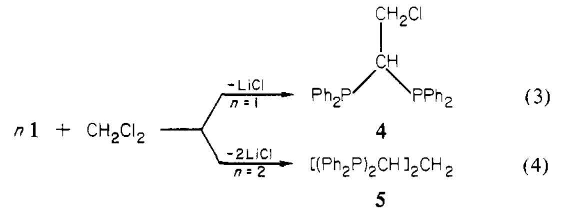
[a] Relative to 85% H_3PO_4 as external standard. [b] Relative to Me_4Si as external standard, with notation of the carbon atoms according to



[c] TMED complex in Et_2O as a solvent. [d] $|J_{AC} + J_{BC}|$. [e] Only a lower limit for J_{PP} could be estimated. [f] Coupling constants are in hertz; the solvent is dichloromethane, if not stated otherwise.



and dichloromethane. According to previous results[1] the chloromethylated bis(phosphine) **4** or the tetrakis(phosphine) **5** were expected to be formed. The adduct of **1** with tetramethylethylenediamine, **1**·TMED,[2] was used in place of **1** for these reactions.

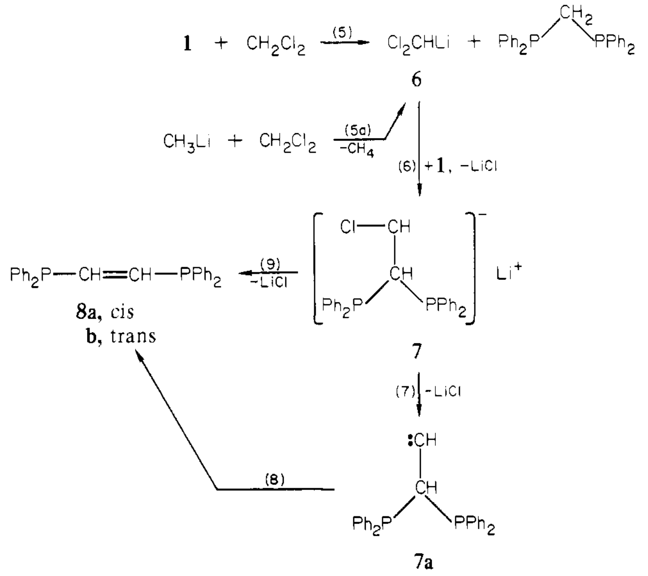


Careful $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopic investigation of the reaction mixture, however, showed that besides the methylene-bridged bis(tertiary phosphine) $Ph_2PCH_2PPh_2$,[3] *cis*- and *trans*-1,2-ethenediylbis(diphenylphosphine)[4,5] were formed. The assignment of the signals was confirmed by comparison with the NMR spectra of independently synthesized bis(phosphines) $Ph_2PCH{=}CHPPh_2$ (**8a**,**b**).[4,5]

Obviously in addition to protonation of **1** insertion of a CH group into the P–C–P skeleton had taken place.

We explain the formation of $(Ph_2P)_2CH_2$ by a proton transfer between **1** and CH_2Cl_2. The carbenoid Cl_2CHLi[6] thus obtained may then react with **1** to form **7**. 1,2-Migration of a Ph_2P group within the carbenoid **7** or the carbene **7a** finally leads to the olefinic bis(phosphines) **8a** and **8b**. This kind of 1,2-rearrangement in carbenes is known to occur in sulfur-substituted derivatives[7] of type $PhCCH_2SR$.

If the reaction of **1** with CH_2Cl_2 is carried out in the presence of an excess of 1 equiv of methyllithium, then according to this scheme $Ph_2PCH_2PPh_2$ should not be formed. This proved to be the case. Only **8a** and **8b** were obtained. The stronger base CH_3Li deprotonates CH_2Cl_2 to give Cl_2CHLi, which then reacts with **1**, forming the olefinic bis(phosphines) **8a** and **8b**.



Dichloromethyllithium has also been obtained by reaction of CH_2Cl_2 and *n*-butyllithium. In the presence of tetrahydrofuran it is stable up to −30 °C. Reaction of olefins with methyllithium/dichloromethane affords cyclopropanes[8] in the temperature range from −20 to +40 °C.

Some comments should be made with respect to the $^{13}C\{^1H\}$ NMR spectra of **8** and **9**. The data given for **8a** and **8b** in the earlier literature either are incomplete[9,10] or result from an incorrect analysis of the spectra.[9] In order to get comparative data, we included in our studies the sulfides **9a** and **9b** of **8a** and **8b**.[11] In a recent publication ^{13}C NMR data of the phosphines **8a** and **8b** were analyzed with use of triple-resonance techniques.[12] Small differences between this set of data and ours may be attributed to concentration and temperature effects.

The ^{13}C nuclei in these compounds represent the X part of an ABX-type spectrum[13] (A, B = ^{31}P, X = ^{13}C), the chemical shift difference between A and B being small. Three-, four-, or five-line patterns are observed depending on the magnitude of J_{AB} relative to $|J_{AX} - J_{BX}|$ or $|J_{AX} - J_{BX}|/2J_{AB}$ for $J_{AB} \neq 0$. 1:2:1 triplets are obtained if $|J_{AB} - J_{BX}|^2 < 8J_{AB}(\Delta\nu_{1/2})$ ($\Delta\nu_{1/2}$ is the line width at half-height).[14] As J_{AB} decreases

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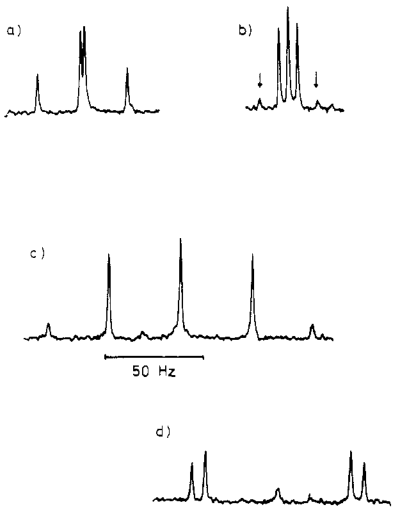

Figure 1. $^{13}C\{^1H\}$ NMR spectra of **8b** and **9a**: (a) vinylic carbon (C1) of **8b**; (b) tertiary carbon (C2) of **8b**; (c) vinylic carbon (C1) of **9a**; (d) tertiary carbon (C2) of **9a**.

a five-line pattern and eventually a four-line pattern will be observed. Parts of the $^{13}C\{^1H\}$ NMR spectra of the compounds **8b** and **9a** are shown in Figure 1a–c.

Experimental Section

All preparations were carried out under an atmosphere of purified nitrogen. Bis(diphenylphosphino)methane was synthesized by a standard literature method.[4] All other chemicals were reagent grade materials.

Reaction of Lithiobis(diphenylphosphino)methane with Dichloromethane. To a solution of 5.0 g (13 mmol) of bis(diphenylphosphino)methane in 50 mL of diethyl ether was added 2 mL of TMED. At room temperature 16 mL (26.7 mmol) of CH_3Li (1.67 M in diethyl ether) was added dropwise. After H_2 evolution was completed, stirring was continued for 1 h. Thereafter the solution was cooled to −78 °C and 1.1 g (13 mmol) of dichloromethane in 25 mL of diethyl ether was added slowly. After 3 h the reaction mixture was allowed to warm up to room temperature, and 10 mL of a saturated aqueous NH_4Cl solution was added with stirring. The water layer was discarded, and the organic layer was evaporated. The crude product was recrystallized from ethanol; yield 4.4 g (85%) of **8a** and **8b** as a 1:1 mixture. The product was characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy.

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Registry No. **8a**, 983-80-2; **8b**, 983-81-3; **9a**, 986-06-1; **9b**, 986-07-2; $Ph_2PCH_2PPh_2$, 2071-20-7.