

is calculated from the equation $RE = (2 + SC) \sum H_{ij}$, where SC is the structure count and the H_{ij} are resonance integrals that correspond to energies for permutations of pairs of electrons over the bonding network. Additional integrals needed for other calculations are $\gamma_2 = 0.34$ eV (conjugated circuit of ten orbitals) and $\omega_2 = -0.26$ eV (conjugated circuit of eight orbitals).

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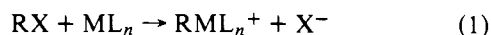
Relative Reactivities of Methyl Iodide and Methyl Tosylate with Transition-Metal Nucleophiles¹

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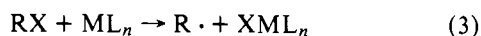
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Abstract: The rate constants k_1 and k_{OTs} are determined for the reaction of methyl iodide and methyl tosylate with a number of transition-metal nucleophiles. The values of k_1 cover a span of 10^{11} in magnitude. The ratio k_1/k_{OTs} covers a range from 10^9 to 10^{-3} , with some nucleophiles not reacting with methyl tosylate before undergoing decomposition. Unfortunately, except for $Co(CN)_5^{3-}$, the ratio cannot be used as a guide to free-radical mechanisms. Except for $Li_2Cu_2Me_4$, Li_2AuMe_2 , and Li_2PtMe_4 , $\log k_1$ plotted against $\log k_{OTs}$ gives a straight line, suggesting a common S_N2 mechanism. The permethylated complexes are unique in having k_1/k_{OTs} less than unity.

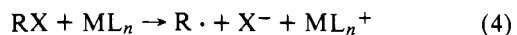
The reactions of transition-metal complexes, ML_n , with alkyl halides and with alkyl sulfonates are of great importance both in the synthesis of organometallic compounds and, by subsequent reactions, in organic synthesis. In these reactions the transition-metal complex acts as a nucleophilic reagent. It can also be regarded as the substrate in a typical oxidative-addition reaction, whether or not both R and X are added to the metal.



Oxidative additions of alkyl halide have been found to occur by a variety of mechanisms.⁴ Simple S_N2 substitution mechanisms are most common, followed by free-radical pathways, next most common. In a few cases concerted addition of RX has been shown to occur.⁵ Two kinds of free-radical paths have been postulated: (a) initiation by attack of the metal atom on the halogen of RX^6



(b) initiation by electron transfer from ML_n^7

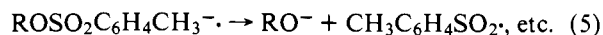


Since the products, and their stereochemistry, often depend critically upon the reaction mechanism, it is important to be able to anticipate which reaction path is likely to be found for a given RX and ML_n . Previous work allows some generalizations to be made.⁸ Free-radical mechanisms become more likely as R varies, primary < secondary < tertiary < benzyl

or allyl. Also free-radical mechanisms are more likely as X changes, $RSO_3^- < Cl^- < Br^- < I^-$.

These observations are useful as far as RX is concerned. However, there is no clear-cut pattern for the role of the metal atom, or its ligands, in predicting the behavior of a given ML_n . In the S_N2 mechanism the metal changes its oxidation state by two units. In the free-radical mechanisms, intermediates or, in some cases, products are formed in which the metal atom changes its oxidation state by only one unit. In some cases this can be a useful guide for prediction. However, transition metals have a variety of oxidation states possible, including unstable ones in the case of intermediates. This makes predictions much more hazardous.

As mentioned above, alkyl sulfonates, such as ROTs, seem reluctant to react by free-radical paths. Powerful electron donors, such as sodium naphthalene, will transfer an electron to an alkyl tosylate.⁹ The products that are formed result from cleavage of the sulfur-oxygen bond.



Such products are not observed in reactions of transition-metal complexes with alkyl sulfonates.

The supposition that alkyl tosylates, or sulfonates, will not react by a free-radical path has been critically tested for one case. The complex $Co(CN)_5^{3-}$ is known to react by halogen abstraction as shown in eq 3.^{6a,8a} The molecules $CH_3O-SO_2C_6H_5$, $CH_3OSO_2C_6H_4CH_3$, and $CH_3CH(OTs)CO_2C_2H_5$ were found not to react with $Co(CN)_5^{3-}$ in 24 h.¹⁰ The corresponding iodides reacted readily and a ratio of $k_1/k_{OTs} > 10^9$ was indicated.

At the start of this work it was also known that $\text{Li}_2\text{Cu}_2\text{Me}_4$ reacted more rapidly with alkyl tosylates than with alkyl iodides.^{10,11} The reactivity ratio k_I/k_{OTs} was only 8.1×10^{-3} for MeI and MeOTs in ether. The rhodium(I) complex $\text{Rh}(\text{C}_2\text{DOBF}_2)$ was known to react more rapidly with MeI than with MeOTs, the ratio k_I/k_{OTs} being 2×10^3 in tetrahydrofuran.¹² In these cases there is strong additional evidence that $\text{S}_{\text{N}}2$ mechanisms are followed.

A range of ratios, k_I/k_{OTs} , is well known for the $\text{S}_{\text{N}}2$ reactions of methyl iodide and methyl tosylate with common nucleophiles. In several solvents, ratios ranging from 5×10^{-3} to 2×10^2 are found.¹³ The pattern is remarkably consistent: soft nucleophiles such as I^- or R_3P give a high ratio, and hard nucleophiles such as OH^- or R_3N give a low ratio. This result has been attributed to a symbiotic stabilization of the transition state when the entering group and the leaving group are both soft or both hard.¹⁴ An equivalent explanation is that the more polar the transition state, the more labile tosylate is as a leaving group compared to iodide.¹⁵ In agreement with this, in poorer solvents k_I/k_{OTs} has been found to increase.

With this background it seemed useful to measure the reactivity ratios, k_I/k_{OTs} , for a number of transition-metal complexes. Failure to react with methyl tosylate, coupled with ready reaction with methyl iodide, would be a criterion for a free-radical mechanism. High ratios might also serve as an index for a tendency to react by such a path. The use of the methyl compounds, of course, would mitigate against free-radical paths. However, methyl free radicals have been found in the reaction of methyl iodide with $\text{Pt}[\text{P}(\text{Ph}_3)]_3$,¹⁶ and the reaction of $\text{Ir}(\text{CO})\text{Cl}[\text{P}(\text{Ph}_3)]_2$ with MeI has one feature which is best explained by a free-radical mechanism, the failure to trap external anions.^{4b}

The use of MeI has another advantage: it allows rate data for transition-metal nucleophiles to be compared with data for other "normal" nucleophiles. Methyl iodide has been used as a test reactant in numerous studies of this kind. The variation of the rate constant as a function of M and L is also of great interest. We still know rather little about the factors which determine reactivity in oxidative-addition reactions.

Experimental Section

Since all the organometallic reagents used in this work were air and water sensitive, procedures involving them were carried out in an atmosphere of dry, prepurified nitrogen or argon. Standard bench-top techniques using Schlenk apparatus and syringes with valves used for synthesis, storage, and kinetics.

¹H NMR spectra were obtained on a Perkin-Elmer R20B, IR spectra on a Perkin-Elmer 283 operated in the absorbance mode, ESR spectra on a Varian E-4, and UV-visible spectra on a Cary 14, and an Applied Photophysics stopped-flow apparatus was used for rapid kinetic experiments.

Solvents were purified by standard literature methods.¹⁷

Methyl iodide was purified by shaking with aqueous NaHSO_3 , washing with water, drying over CaCl_2 , and distilling under nitrogen from copper wool. The distillate was stored in the dark in a needlepoint flask over copper wire.

Methyl *p*-toluenesulfonate was purified by distillation under reduced pressure or by refluxing over, and distilling from, tribenzylamine under reduced pressure. The distillate was stored in the dark under nitrogen in a needlepoint flask.

The following compounds were prepared by methods in the literature: $[\text{CpMo}(\text{CO})_3]_2$,¹⁸ $\text{NaCpCr}(\text{CO})_3$,^{19,20} $\text{NaCpW}(\text{CO})_3$,¹⁹ $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$,²¹ $\text{Co}(\text{dmg})_2(\text{pyr})$,²³ $\text{NaCo}(\text{dmg})_2(\text{pyr})$,²⁴ $\text{Na}_3\text{Rh}(\text{CN})_4$,²⁵ $\text{Ni}(\text{PPh}_3)_3$,²⁶ $\text{NiI}(\text{PPh}_3)_3$,²⁷ $\text{Pd}(\text{PPh}_3)_3$,²⁸ $\text{Pd}(\text{PET}_3)_3$,²⁹ $\text{Pt}(\text{PPh}_3)_3$,³⁰ $\text{Pt}(\text{PMe}_2\text{Ph})_4$,³¹ $\text{Pt}(\text{PET}_3)_3$,³¹ $\text{Ni}(\text{PET}_3)_4$,³² $\text{PtI}_2(\text{PMe}_2\text{Ph})_2$,³¹ *cis*- $\text{PtCl}_2(\text{PMe}_2\text{Ph})_2$,³³ *cis*- $\text{PtMe}_2(\text{PMe}_2\text{Ph})_2$,³³ *trans*- $\text{PtI}(\text{Me})(\text{PMe}_2\text{Ph})_2$,³³ Li_2PtMe_4 ,³⁴ $\text{AuCl}(\text{PPh}_3)_3$,³⁵ and $\text{LiAu}(\text{CH}_3)_2$.³⁶

Transition-metal complexes of the type $\text{NaCpM}(\text{CO})_x$ ($x = 1, 2, 3$) or $\text{NaM}(\text{CO})_y$ ($y = 4, 5$), with the exception of $\text{NaCpCr}(\text{CO})_3$ and $\text{NaCpW}(\text{CO})_3$, were made by the reduction of the dimer in THF or dimethoxyethane with sodium amalgam, followed by filtration. Li

analogues were prepared similarly, except Li wire was used as the reductant. The dimers were purchased from Pressure Chemical Co., Pittsburgh, Pa.

All reagents and products were characterized by comparison of experimental spectra with published spectra.

Kinetic Studies. All reactions were carried out under an atmosphere of prepurified nitrogen or argon. In general, a concentrated solution of MeI or MeOTs was added to a solution of the metal complex, such that the volume change was negligible compared to the total volume, to give pseudo-first-order conditions or second-order, equal concentration conditions. All kinetic experiments were at least duplicated. Where the reactions had been previously shown to be second order, first order in both metal complex and alkyl halide, variation in reactant concentrations was not always made. Otherwise suitable variations in concentration were made to determine the rate law.

Temperatures were controlled to ± 0.5 (0–40 °C) and ± 1.0 °C (<0 °C) on the Perkin-Elmer R20-B and to ± 0.1 °C on the Cary 14 and Perkin-Elmer 283, and were ambient (24 ± 1 °C) on the stopped-flow apparatus. Activation parameters were obtained by determining the second-order rate constant, k_2 , at three temperatures separated by a minimum total of 20 °C. Plots of $\ln k_2$ were linear with $1/T$.

The reaction of $\text{NaCpCr}(\text{CO})_3$ with MeI in THF at 5, 15, 25, and 35 °C was monitored by following the rate of disappearance of the reactant Cp NMR signal. A 0.12 M solution of $\text{NaCpCr}(\text{CO})_3$ (250 μL) was injected into a serum-capped NMR tube which had been flushed with nitrogen. The tube was then placed into the NMR probe and the temperature allowed to equilibrate. The tube was withdrawn, 50 μL of a 0.603 M solution of MeI in THF was injected into the tube, and the tube was shaken and placed back into the probe. There was rapid establishment of temperature equilibrium due to the rapid spinning of the tube.

For second-order kinetics with nearly equal concentrations of reactants, the integrated rate equation is

$$1/(d-x) - 1/d = kt \quad (6)$$

where d is the mean initial concentration, x is the decrease in concentration of a reactant in a given time, and k is the second-order rate constant. Multiplying by d gives $d/(d-x)$, which is equivalent to A_0/A_t . Thus a plot of A_0/A_t vs. t will have a slope equal to dk . For an NMR peak, the area under the curve is the absorbance. The area may be approximated by the product of the height times the full width at half-height.

A similar procedure was followed for the reaction of MeOTs with 0.12 M $\text{NaCpCr}(\text{CO})_3$ at 15, 25, 35, and 45 °C in THF under pseudo-first-order conditions.

The NMR method was also used to follow the reaction between 0.16 M $\text{NaCpMo}(\text{CO})_3$ and MeOTs and 0.19 M $\text{NaCpMo}(\text{CO})_3$ and MeI in THF. Here the rate of appearance of $\text{CpMoMe}(\text{CO})_3$ was followed by monitoring the rate of appearance of the Mo-Me peak. Pseudo-first-order conditions were maintained for the MeOTs reaction at 15, 25, and 35 °C. The MeOTs reaction was also run in DME at 35 °C. The MeI reaction was run under second-order conditions at –50 and –30 °C. In this case the quantity $d/(d-x) - 1$ is equivalent to $x/(d-x)$. Here x would be the amount of Mo-Me formed. In terms of absorbance, a plot of $A_t/(A_\infty - A_t)$ vs. t would have a slope equal to dk .

The reaction between 0.16 M $\text{NaCpW}(\text{CO})_3$ and MeOTs at 5, 15, 25, and 35 °C in THF was followed as in the case of $\text{NaCpMo}(\text{CO})_3$.

The reaction between $\text{NaCpW}(\text{CO})_3$ and MeI in THF under second-order conditions was monitored by following the appearance of $\text{CpWMe}(\text{CO})_3$ at 218 cm^{-1} in the IR. $\text{NaCpW}(\text{CO})_3$ (15.0 mL of 1.6×10^{-3} M) was placed in a nitrogen-flushed serum-capped flask which was fitted with a magnetic stirrer. The flask was placed in a bath and the temperature allowed to equilibrate. Then approximately 300 μL of a MeI solution was injected with rapid stirring. By means of a pressure differential, the solution was transferred into a low-temperature IR cell. This transfer took less than 5 s. A variable path length IR cell filled with THF was placed in the reference beam to give a flat base line in the region of interest. In this case, the quantity $d/(d-x)$ is equivalent to $A_\infty/(A_\infty - A_t)$. The reaction was run under second-order conditions at 0.0 and 25.0 °C, and under pseudo-first-order conditions at –15.0 °C.

For the reaction between 2.0×10^{-3} M $\text{NaMn}(\text{CO})_5$ and MeOTs in THF a water-jacketed IR cell was used instead of a low-temperature cell. Coolant (water or water-methanol) was pumped continuously

through the system. Transfer was made from the reaction vessel to the IR cell in less than 5 s by means of a polyethylene air-tight syringe. The rate of formation of $\text{MeMn}(\text{CO})_5$ was followed by monitoring the growth of the IR band at 2010 cm^{-1} . The reaction was run under pseudo-first-order conditions at 25.3, 37.5, and 49.5 °C.

The reaction between $2.0 \times 10^{-3}\text{ M NaMn}(\text{CO})_5$ and MeI in THF was run under second-order conditions at 0.0, 25.1, and 37.6 °C, and was performed as above.

The reaction between $2.0 \times 10^{-3}\text{ M NaRe}(\text{CO})_5$ and MeOTs in THF was monitored by following the disappearance of the anion at 1864 cm^{-1} . The reaction was carried out under pseudo-first-order conditions at 10.2, 25.2, and 36.3 °C. The reaction between the anion and MeI was too fast to follow.

The reaction of $5.0 \times 10^{-3}\text{ M NaCo}(\text{CO})_4$ and MeI in THF was run under pseudo-first-order conditions at 10.2, 17.5, and 25.1 °C, and was monitored by following the increase in absorbance in the UV-visible due to the formation of $\text{MeCo}(\text{CO})_4$. Typically, 4.0 mL of anion solution was put into a nitrogen-flushed needle-point UV-visible cell, the cell allowed to come to temperature equilibrium, and 100 μL or less of MeI solution injected into the cell and the cell was shaken. The cell was then placed into the spectrophotometer and the absorbance monitored. The reaction of $\text{NaCo}(\text{CO})_4$ and MeOTs in THF was run similarly.

The reaction of $4.0 \times 10^{-3}\text{ M Na}_3\text{Co}(\text{CN})_5$ with MeI at 17.4, 25.0, 33.1, and 40.9 °C in 20% water–80% methanol (v/v), ionic strength of 0.20 M NaClO_4 , was carried out under pseudo-first-order conditions, and was monitored by following the decrease in $\text{Na}_3\text{Co}(\text{CN})_5$ at 975 nm. Our rate constant at 25 °C is two to three times as large as that reported earlier at a lower ionic strength (0.02 M).^{8a}

The reaction of $5 \times 10^{-3}\text{ M Na}[\text{Co}(\text{dmg})_2\text{pyr}]$ with MeI and MeOTs in 0.10 M methanolic NaOH at 25 °C under pseudo-first-order conditions was followed by monitoring the disappearance of the Co(I) species at 650 nm on a stopped-flow apparatus. The solvolysis of MeI is negligible for the duration of the kinetic measurements under these conditions; however, the rate of solvolysis of MeOTs is not. The rate of solvolysis was followed by monitoring the disappearance of MeOTs at 277.5 nm. A fresh solution of MeOTs was prepared for the reaction with the Co(I) species, and each stopped-flow run was timed with reference to this preparation. The MeOTs concentration could then be easily calculated at any time through the usual exponential relationship.

The reaction of $1.9 \times 10^{-4}\text{ M Na}_3\text{Rh}(\text{CN})_4$ with MeI and methyl benzenesulfonate at 25 °C under pseudo-first-order conditions in 0.30 M aqueous NaOH was followed by monitoring the disappearance of the Rh(I) species at 322.5 nm on a stopped-flow apparatus. MeOTs is quite insoluble in water; thus it was necessary to use MeBs. The problem of hydrolysis of MeBs was handled as above. MeBs is only slightly more reactive than MeOTs.

The reaction of $5 \times 10^{-4}\text{ M NaCpFe}(\text{CO})_2$ with MeOTs at 25 °C in THF under pseudo-first-order conditions was followed by monitoring the disappearance of the anion at 425 nm using a stopped-flow apparatus. The rate of addition of MeI was too fast to measure.

The reaction of $1.0 \times 10^{-2}\text{ M NaCpNi}(\text{CO})$ with MeOTs at 25 °C in THF under second-order conditions was too fast to follow by monitoring the change in the carbonyl stretching region. There was no significant change in the UV-visible region that could be used in monitoring the reaction.

The reaction of $1.0 \times 10^{-4}\text{ M Ni}(\text{PPh}_3)_3$ with MeI at 25.0 °C in benzene was carried out under second-order conditions and unequal concentrations, and was monitored by following the decrease in absorbance of the $\text{Ni}(\text{PPh}_3)_3$ species at 385 nm.

The reaction of $5 \times 10^{-4}\text{ M Pd}(\text{PPh}_3)_3$ with MeI at 17.4, 25.1, 33.6, and 42.4 °C in benzene under pseudo-first-order conditions was followed by monitoring the decrease in absorbance of $\text{Pd}(\text{PPh}_3)_3$ at 410 nm. An attempt was made to follow the reaction of MeOTs with $\text{Pd}(\text{PPh}_3)_3$, but, owing to the decomposition of $\text{Pd}(\text{PPh}_3)_3$ in solution, no conclusive results were obtained.

The rate of reaction of $\text{Pt}(\text{PPh}_3)_3$ and MeOTs in benzene at 25.0 °C under pseudo-first-order conditions was determined by following the decay of $\text{Pt}(\text{PPh}_3)_3$ at 410 nm. The reactions were followed only to approximately 5% conversion.

The reaction of $5 \times 10^{-4}\text{ M Pt}(\text{PPh}_3)_4$ with MeI at 17.4, 25.1, 33.6, 42.4, and 48.7 °C in benzene under pseudo-first-order conditions was followed by monitoring the decrease in absorbance due to $\text{Pt}(\text{PPh}_3)_4$ at 410 nm.

The reaction of $4.8 \times 10^{-4}\text{ M Ni}(\text{PET}_3)_4$ with MeOTs in benzene

under argon at 5.5, 15.1, and 25.3 °C was carried out under second-order conditions by following the decrease in absorbance of $\text{Ni}(\text{PET}_3)_4$ at 503 nm. The reaction with MeI was too fast to follow on the stopped-flow apparatus.

The reaction of $3.1 \times 10^{-3}\text{ M Pd}(\text{PET}_3)_3$ with MeOTs in benzene at 25.0, 31.9, 41.1, and 48.7 °C under pseudo-first-order conditions was followed by monitoring the decrease in absorbance due to $\text{Pd}(\text{PET}_3)_3$ at 370 nm. The reaction with MeI at 25 °C in benzene under second-order conditions was run on the stopped-flow apparatus.

The reaction of $2 \times 10^{-3}\text{ M Pt}(\text{PET}_3)_3$ with MeOTs at 17.4, 25.2, 33.1, and 43.5 °C in benzene under pseudo-first-order conditions was followed by monitoring the decrease in absorbance of $\text{Pt}(\text{PET}_3)_3$ at 381 nm.

The reaction of $9.0 \times 10^{-4}\text{ M Pt}(\text{PET}_3)_3$ with MeI at 14.5, 25.0, 33.4, and 41.1 °C in benzene under second-order conditions was followed as above. $\text{Pt}(\text{PET}_3)_3$ (2.0 mL of $2.0 \times 10^{-3}\text{ M}$) was allowed to reach temperature equilibrium in a thermostated UV-visible cell, and then 2.0 mL of $1.8 \times 10^{-3}\text{ M}$ MeI was withdrawn by syringe from a thermostated flask and injected into the cell. This allows mixing times of less than 5 s to be achieved with the Cary 14.

The rate of reaction of 0.10 M LiAuMe_2 with MeI in diethyl ether at -30 , -20 , -10 , and 0 °C under second-order conditions was determined by following the decrease of the LiAuMe_2 NMR signal. The rate of reaction of LiAuMe_2 with MeOTs was too fast to follow under second-order conditions, even using UV spectroscopy.

The reaction between 0.17 M $\text{IrCl}(\text{CO})(\text{PMe}_2\text{Ph})_2$ and 0.63 M MeOTs in benzene at 25 °C was monitored by following the growth of the Ir–Me peak in the NMR. The reaction was carried out in a sealed NMR tube.

The reaction of $2.0 \times 10^{-4}\text{ M IrCl}(\text{CO})(\text{PPh}_3)_2$ with MeI in benzene was followed under pseudo-first-order conditions at 25 °C. The change in absorption at 387 nm was monitored. The reaction with MeOTs was too slow to measure.

The reaction of $5 \times 10^{-3}\text{ M cis-PtMe}_2(\text{PMe}_2\text{Ph})_2$ with MeI at 25.0, 36.0, and 46.5 °C in benzene under pseudo-first-order conditions was monitored by following the disappearance of $\text{cis-PtMe}_2(\text{PMe}_2\text{Ph})_2$ in the ultraviolet.

The reaction of $1.0 \times 10^{-3}\text{ M trans-PtIme}(\text{PMe}_2\text{Ph})_2$ with MeI at 25.0, 36.0, 46.5, and 55.0 °C in benzene under pseudo-first-order conditions was monitored by following the appearance of the product, $\text{PtI}_2\text{Me}_2(\text{PMe}_2\text{Ph})_2$, in the ultraviolet.

The reaction of 0.0715 M $\text{PtI}_2(\text{PMe}_2\text{Ph})_2$ with 0.357 M MeOTs and MeI, the reaction of 0.19 M $\text{trans-PtIme}(\text{PMe}_2\text{Ph})_2$ with 0.26 M MeOTs, and the reaction of 0.39 M $\text{cis-PtMe}_2(\text{PMe}_2\text{Ph})_2$ and 0.39 M MeOTs were carried out in a sealed NMR tube. For the $\text{cis-PtMe}_2(\text{PMe}_2\text{Ph})_2$ reaction, the decrease in the methyl ester peak of MeOTs was followed.

The relative rates of reaction of MeI and MeOTs with Li_2PtMe_4 were obtained in the following manner: 25.5 mg (0.077 mmol) of $\text{PtMe}_2(\text{COD})$ was placed in an NMR tube and purged. MeLi (500 μL of 0.50 M) was added at 0 °C, the solution warmed to room temperature, and the tube shaken. The tube was then cooled to -20 °C and the Li_2PtMe_4 allowed to precipitate. The ether was syringed off and the crystals were washed with 500 μL of ether. After the ether was syringed off, the crystals were dried under vacuum. Diethyl ether-*d*₁₀ (250 μL) was then added and the spectrum recorded. The solution was cooled to 0 °C, and a solution containing 12.0 μL of MeOTs (0.077 mmol) and 4.8 μL of MeI (0.077 mmol) was then injected. The tube was shaken and the NMR spectrum recorded as soon as possible. The MeI and MeOTs methyl peaks were measured.

Results

Rate data and activation parameters for the reactions of methyl iodide and methyl tosylate with a number of transition-metal complexes are given in Table I. Unfortunately, experimental difficulties made it impossible to measure all rates in common solvent. The choice of solvent was dictated by two factors: (a) syntheses had been reported in these solvents; (b) previous studies, including product identification and kinetic measurements for MeX, had been made in these solvents. For each complex the ratio k_1/k_{OTs} always refers to the same solvent and temperature for both reactants.

Plots of the appropriate concentration factor were linear for

Table I. Rate Data and Activation Parameters for Reaction of MeI and MeOTs with Transition-Metal Nucleophiles

compd	$k_2, \text{M}^{-1} \text{s}^{-1}, 25^\circ \text{C}$		solvent	$\Delta H^\ddagger, \text{kcal mol}^{-1}$		$\Delta S^\ddagger, \text{cal mol}^{-1} \text{K}^{-1}$	
	MeI	MeOTs		MeI	MeOTs	MeI	MeOTs
CpCr(CO) ₃ ⁻	7.5×10^{-2}	2.6×10^{-3}	THF	11.0	15.0	-26.7	-20.2
CpMo(CO) ₃ ⁻	1.5	1.6×10^{-3}	THF	5.7	20.5	-39	-2.5
CpW(CO) ₃ ⁻	2.4	1.6×10^{-3}	THF	10.4	24.6	-22.1	11.3
Mn(CO) ₅ ⁻	7.4	1.7×10^{-2}	THF	9.1	20.8	-24.2	2.9
LiMn(CO) ₅	7.1	3.0×10^{-2}	THF				
Re(CO) ₅ ⁻	(1000) ^a	1.0	THF		24.7		24.4
IrCl(CO)(PPh ₃) ₂	1.0×10^{-3}	NR	benzene	5.6 ^d		-51 ^d	
IrCl(CO)(PMe ₂ Ph) ₂	5.0×10^{-3}	6.7×10^{-6}	benzene				
Co(CO) ₄ ⁻	4.37×10^{-2}	$<3 \times 10^{-3}$	THF	15.1		-14.0	
Co(CN) ₅ ⁻³	2.52×10^{-2}	NR	H ₂ O-MeOH	12.0		-27.6	
Co(dm _g) ₂ pyr ⁻	1.8×10^4	14.4	alc NaOH				
Rh(CN) ₄ ³⁻	7.8×10^2	2.6 ^b	aq NaOH				
CpFe(CO) ₂ ⁻	(2.8×10^6) ^a	2.4×10^2	THF				
CpNi(CO) ⁻	(2.2×10^5) ^a	>30	THF				
Ni(PPh ₃) ₃	2.1×10^2	NR	benzene				
Pd(PPh ₃) ₃	3.09×10^{-2}	NR	benzene	17.8		-5.9	
Pt(PPh ₃) ₃ ^e	1.1×10^{-2}	3.0×10^{-6}	benzene	16.1		-14.6	
Ni(PEt ₃) ₄	$>8 \times 10^5$	2.6	benzene		12.2		-15.9
Pd(PEt ₃) ₃	1.3×10^3	1.51×10^{-3}	benzene		21.3		-0.1
Pt(PEt ₃) ₃	9.7	4.4×10^{-4}	benzene	15.3	15.0	-2.3	-23.8
LiAuMe ₂	1.3×10^{-1}	>20	Et ₂ O	6.4		-41	
Li ₂ PtMe ₄	(0.16) ^c	>0.5	Et ₂ O				

^a Estimated from data in ref 37. See text. ^b The reagent is methyl benzenesulfonate; see text. ^c Estimated from data in ref 34. ^d From ref 40. ^e The reactants are a mixture of Pt(PPh₃)₂ and Pt(PPh₃)₃; see ref 39.

2-3 half-lives for pseudo-first-order reactions, and at least for 1 half-life under reactions run under second-order conditions. In all cases except as mentioned next, the second-order rate law was found:

$$\text{rate} = k_2[\text{MeX}][\text{complex}] \quad (7)$$

For the reactions of IrCl(CO)(PPh₃)₂ with MeI, and Mn(CO)₅⁻, Re(CO)₅⁻, and Pt(PEt₃)₃ with MeOTs, k_2 was not constant with changing MeX concentration. The values at infinite dilution were used in these cases. The variations were not large and presumably resulted from changes in solvent polarity. For example, the rate constant for IrCl(CO)(PPh₃)₂ with MeI was $1.0 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$ at infinite dilution. At 1 M MeI the value was 3.3×10^{-3} , in agreement with values reported by others^{40,44,53} at similar concentrations.

The values in parentheses for MeI reaction with Re(CO)₅⁻, CpFe(CO)₂⁻, and CpNi(CO)⁻ were literature values corrected for a solvent effect. The original data was obtained in dimethoxyethane (glyme).³⁷ In four other cases we found the rate in THF to be two to nine times faster than in diglyme. An average ratio of 4 was used to correct the data for the above complexes.

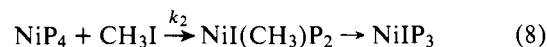
The reactions of the phosphine complexes of Ni(0), Pd(0), and Pt(0) are complicated by dissociation of the phosphine ligands to produce species which are more reactive. For example, Pt(PPh₃)₄ dissociates to Pt(PPh₃)₃ and Pt(PPh₃)₂, which are the actual reactants with MeI.³⁹ To minimize this effect the tris complexes (MP₃) were used as reagents, when possible. For both P = PPh₃ and PEt₃, these would be the dominant species in solution at the concentrations used. It is possible that Pd(PPh₃)₂ and Ni(PPh₃)₂ are also present. If so, their contributions to the rates have not been unraveled. Apparently the bis complexes do not form when P = PEt₃.⁵⁴

With the exception of the reaction of MeI with Ni(PPh₃)₃ and of MeOTs with Co(CO)₄⁻ and Pt(PPh₃)₃, the products corresponded to the methylated complexes as established by NMR and IR spectra and in agreement with previous reports in the literature. The reactions of MeOTs with M(PEt₃)_{3,4}, M = Ni, Pd and Pt, produced the trans adduct M(OTs)-Me(PEt₃)₂, as established by the phosphine and methyl splitting patterns in the NMR spectra.

The reaction of MeOTs with Pt(PPh₃)₃, which was very slow, was followed only to 5% completion. The product presumably was [PtMe(PPh₃)₃]⁺, which is formed when the more reactive methyl fluorosulfonate is used.³⁸ The initial rate was found to be first order in both MeOTs and complex concentration.

The reaction of MeI with Co(CO)₄⁻ showed good kinetic behavior, though a slow decomposition of the product, CH₃Co(CO)₄, was noted. The reaction with CH₃OTs gave nonlinear plots of $\ln(A_t - A_\infty)$ vs. time, and the maximum absorbance obtained increased with increasing MeOTs concentration. The rate constant reported is for the initial rate.

When MeI reacted with Ni(PPh₃)₃ or Ni(PPh₃)₄ at room temperature, the product was NiI(PPh₃)₃, as shown by its ESR spectrum. This was observed at liquid nitrogen temperature in toluene, for a reaction mixture of Ni(PPh₃)₄ with MeI, and for a sample of NiI(PPh₃)₃ prepared according to the literature.^{27a} In both cases a single broad line was found at a g value of 2.223 ± 0.002 . It is tempting to correlate this unusual product with the free-radical mechanism (3) and the high rate of reaction. However, when the reaction was run at -30°C , the NMR spectrum showed a methyl triplet at τ 9 and with $\nu = 14 \text{ Hz}$. Upon warming, this spectrum disappeared. Thus it appears that the reaction sequence is that suggested by Otsuka:^{27b}



The rate law (7) was followed at room temperature.

The reaction of IrCl(CO)(PPh₃)₂ and M(PPh₃)_{3,4} with methyl tosylate is very slow, or unobservable, before decomposition of the complex occurs. It seemed possible that this might be the result of an unfavorable equilibrium:



To test this possibility a benzene solution (containing some acetone) of PtMe(PPh₃)₃SO₃F and (Bu₄N)OTs was prepared. After several days, no evidence for the reversal of (9) was seen in the vis-UV spectrum. Therefore reaction of Pt(PPh₃)_{3,4} with MeOTs is simply very slow.

The effect of the methyl ligand on the tendency of Pt(II) to

Table II. Effect of Methylation on Rates of Reaction of Methyl Iodide and Methyl Tosylate with Platinum(II) Complexes at 25 °C

complex	$k_2, \text{M}^{-1} \text{s}^{-1}$		solvent
	MeI	MeOTs	
PtI ₂ L ₂ ^a	NR	NR	C ₆ H ₆
<i>trans</i> -PtI ₂ MeL ₂	4.5×10^{-6}	NR	C ₆ H ₆
<i>cis</i> -PtI ₂ Me ₂ L ₂	3.1×10^{-3}	1.7×10^{-6}	C ₆ H ₆
Li ₂ PtMe ₄	0.16	>0.5	Et ₂ O

^a L = PMe₂Ph.**Table III.** Nucleophilic Reactivities Based on k_1 and k_1/k_{OTs} Ratios for Transition-Metal Nucleophiles at 25 °C

	k_1	k_1/k_{OTs}	solvent
CpFe(CO) ₂ ⁻	2.8×10^6	1.2×10^4	THF
Ni(PET ₃) ₄	$>8 \times 10^5$	3×10^5	C ₆ H ₆
CpRu(CO) ₂ ^{- a}	3×10^5		THF
CpNi(CO) ⁻	2.2×10^5	$<1 \times 10^4$	THF
Co(dmg) ₂ pyr ⁻	1.8×10^4	1.2×10^3	MeOH
Pd(PET ₃) ₃	1.3×10^3	8.6×10^5	C ₆ H ₆
Rh(CN) ₄ ³⁻	7.8×10^2	300	H ₂ O
Re(CO) ₅ ⁻	1×10^3	1×10^3	THF
Fe(CO) ₄ ^{2- b}	5×10^2	88	THF
Ni(PPh ₃) ₃	2.1×10^2	large	C ₆ H ₆
Rh ^I (C ₂ DOBF ₂) ^c	$>1 \times 10^2$	$>2 \times 10^3$	THF
Pt(PET ₃) ₃	9.7	2.2×10^4	C ₆ H ₆
Mn(CO) ₅ ⁻	7.4	430	THF
CpW(CO) ₃ ⁻	2.4	1.5×10^3	THF
CpMo(CO) ₃ ⁻	1.5	940	THF
[LiCuMe ₂] ₂ ^d	1.46	8.1×10^{-3}	Et ₂ O
Li ₂ PtMe ₄	1.6×10^{-1}	<0.3	Et ₂ O
LiAuMe ₂	1.3×10^{-1}	$<5 \times 10^{-3}$	Et ₂ O
CpCr(CO) ₃ ⁻	7.5×10^{-2}	29	THF
Co(CO) ₄ ⁻	4.37×10^{-2}	>15	THF
Pd(PPh ₃) ₃	3.09×10^{-2}	large	C ₆ H ₆
Co(CN) ₅ ³⁻	2.52×10^{-2}	>10 ⁸	MeOH-H ₂ O
CpIr(CO)PPh ₃ ^e	4.8×10^{-3}		THF
Pt(PPh ₃) ₃	1.1×10^{-2}	3.7×10^3	C ₆ H ₆
CpRh(CO)PPh ₃ ^e	8×10^{-4}		THF
IrCl(CO)(PPh ₃) ₂	1.0×10^{-3}	large	C ₆ H ₆
CpCo(CO)PPh ₃ ^e	6×10^{-4}		THF
RhCl(CO)(PPh ₃) ₂ ^f	3.6×10^{-5}		MeI
PhS ^{- a}	1×10^5	7.7	THF
PPh ₃ ^g	6×10^{-5}	7.7	Et ₂ O

^a Reference 37. Rate in DME multiplied by 4 to convert to THF.^b Reference 41. Rate of *n*-decyl iodide multiplied by 100 to convert to methyl iodide. ^c Reference 12. The ligand C₂DOBF₂ has four N donor atoms. ^d Reference 10. ^e Reference 42. Solvent correction applied to Rh and Ir based on Co. ^f Reference 43. ^g Reference 35.

give oxidative addition is shown in Table II. Successive replacement of iodide or phosphine by methyl causes a steady increase in reactivity. MeI is more reactive than MeOTs, except for Li₂PtMe₄.

Discussion

Table III summarizes the rate data for the complexes studied in this work, and also shows some additional results from the literature. The rate constant for reaction with methyl iodide is given as a measure of nucleophilic reactivity. Also the ratio, k_1/k_{OTs} , is given when it is known. Two non-transition-metal nucleophiles, PhS⁻ and PPh₃, are added for reference.

It has been necessary to give data in several different solvents, unfortunately. Some additional information on the effect of the solvent on rates may be helpful. Most neutral complexes have been studied in benzene, in this and other work. MeI reacts three times faster with Vaska's compound in THF than it does in benzene.⁴⁴ Also, (*n*-Pr)₃N reacts with MeI 1.5 times faster in THF than in benzene.⁴⁵ This reaction, in fact, is

slightly faster in THF than in methanol. Neutral nucleophiles usually react considerably faster in methanol or THF than in ether. For example, PPh₃ reacts with MeI 45 times faster in methanol than in ether.³⁵ Neutral nucleophiles react with MeI several times faster in water than in methanol.⁴⁶

A comparison of reactivity of an anion in THF or Et₂O with methanol or water is more difficult. There are two opposing effects. From simple electrostatic considerations, a free anion would be more reactive in a medium of low dielectric constant. This shows up in the high reactivity of PhS⁻ as the (*n*-Bu)₄N⁺ salt in glyme.³⁷ This figure, corrected to THF, has $k_1 = 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ in Table III. The corresponding figure for methanol is $k_1 = 1.07$.⁴⁷ However, with Na⁺ or Li⁺ there is extensive ion pairing of transition-metal anions in solvents such as THF.^{41,48} These ion pairs can be much less reactive than the free ions. In this case a more polar solvent will release the more reactive anion and rates can actually increase compared to the less polar solvent.

The effect shows up strongly in the reactivity of Na₂Fe(CO)₄.⁴¹ In THF the reactive species is the tight ion pair NaFe(CO)₄⁻. In *N*-methylpyrrolidinone (NMP), a dipolar aprotic solvent, the active species is the solvent-separated ion pair, Na⁺:S:Fe(CO)₄²⁻, which is 20 000 times more reactive than NaFe(CO)₄⁻. In methanol the rate might be similar to that in NMP, though hydrogen bonding to the oxygen atoms of the anion would reduce the reactivity.

With these remarks in mind, it is not easy to say which nucleophile in Table III is most reactive. The apparent winner, CpFe(CO)₂⁻, has the advantage of being a tetrabutylammonium salt in THF, whereas Fe(CO)₄²⁻ is the sodium salt, actually NaFe(CO)₄⁻. Another candidate for top nucleophile in the transition-metal family is the cobalt(I) species, vitamin B₁₂.²⁴ This is several times more reactive than Co(dmg)pyr⁻, shown in Table III. From the rate constant for Na⁺:S:Fe(CO)₄²⁻ in NMP, a value of about $10^6 \text{ M}^{-1} \text{ s}^{-1}$ in methanol may be estimated. This is to be compared to a measured value of 3.4×10^4 for vitamin B₁₂.

As far as the role of the metal on the tendency to undergo oxidative addition is concerned, only similar complexes can be compared. The data in Table III give the orderings Ni(0) \gg Pd(0) \gg Pt(0) and Fe(0) $>$ Ru(0), with Ni(PET₃)₄ being extremely reactive for a neutral species.⁴⁹ There are also the orderings Re(-I) $>$ Mn(-I), Ir(I) $>$ Rh(I) $>$ Co(I), and W(0) \sim Mo(0) $>$ Cr(0). Apparently there is no simple rule for stating whether the first, second, or third transition series is most reactive.

The range of reactivities covered in Table III is quite large, about 10¹¹. This may be compared to the range for normal nucleophiles in methanol,⁴⁷ which is about 10¹⁴. This range includes the most reactive non-transition-metal nucleophiles, Ph₂Bi⁻, Ph₂As⁻, and Ph₂Sb⁻, as estimated from their reactivities in glyme.³⁷ The latter examples are about 10³ times more reactive than CpFe(CO)₂⁻.

The ratio k_1/k_{OTs} is unusually large for transition-metal nucleophiles, except for three curious exceptions. These are the permethylated species Li₂Cu₂(CH₃)₄, LiAu(CH₃)₂, and Li₂Pt(CH₃)₄. It is quite unexpected that k_1/k_{OTs} is less than unity in these cases. As mentioned earlier, such a low ratio has been found only for hard nucleophiles previously.¹³ These complexes have soft metal atom centers and soft ligands and would be considered as supersoft nucleophiles. Only the permethylated species show abnormal reactivity with MeOTs, as seen in Table II.

The solvent is ethyl ether in the three cases mentioned. It has been noted that in THF alkyl halide and alkyl tosylate react at comparable rates with Li₂Cu₂Me₄, but that tosylates are more reactive than iodides in ether.¹¹ Thus there is a bias in ether for k_{OTs} . However, triphenylphosphine has a normal k_1/k_{OTs} ratio of 7.7 in ether.³⁵

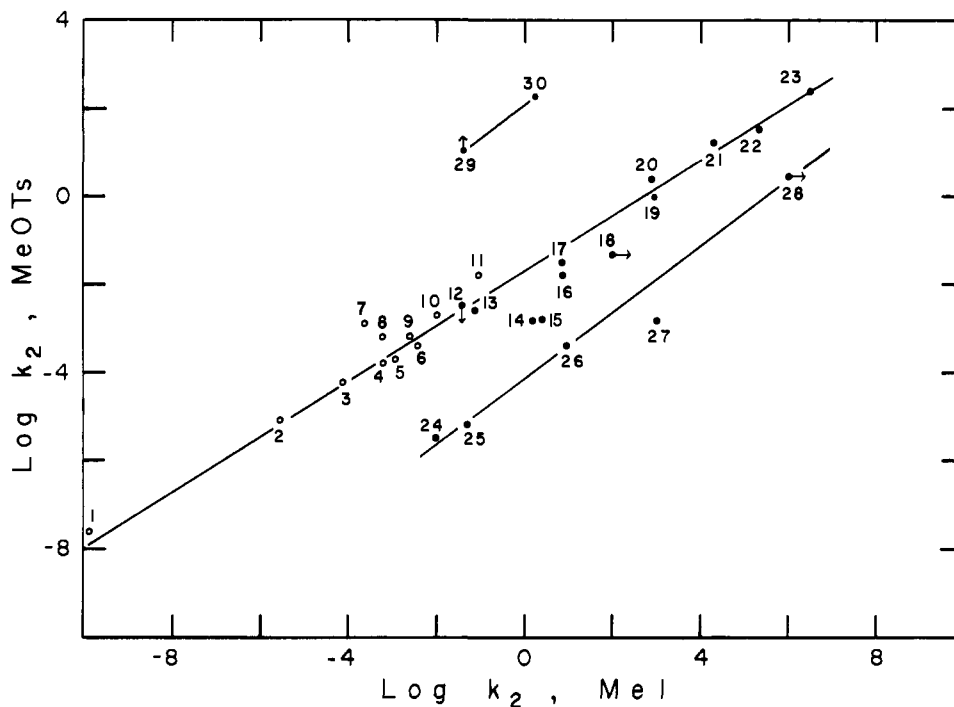


Figure 1. Plot of $\log k_{OTs}$ vs. k_1 with nonmetal (O) and transition-metal (●) nucleophiles: 1, MeOH; 2, Cl^- ; 3, Br^- ; 4, SCN^- ; 5, PPh_3 ; 6, I^- ; 7, MeO^- ; 8, Et_3N ; 9, $CS(NH_2)_2$; 10, $SeCN^-$; 11, $C_6H_5S^-$; 12, $Co(CO)_4^-$; 13, $CpCr(CO)_3^-$; 14, $CpMo(CO)_3^-$; 15, $CpW(CO)_3^-$; 16, $Mn(CO)_5^-$; 17, $LiMn(CO)_5$; 18, $Rh(C_2DOBF_2)$; 19, $Re(CO)_5^-$; 20, $Rh(CN)_4^{3-}$; 21, $Co(dmg)_2pyr^-$; 22, $CpNi(CO)^-$; 23, $CpFe(CO)_2^-$; 24, $Pt(PPh_3)_3$; 25, $IrCl(CO)(PMe_2Ph)_2$; 26, $Pt(PEt_3)_3$; 27, $Pd(PEt_3)_3$; 28, $Ni(PEt_3)_4$; 29, $LiAuMe_2$; 30, $[LiCuMe_2]_2$.

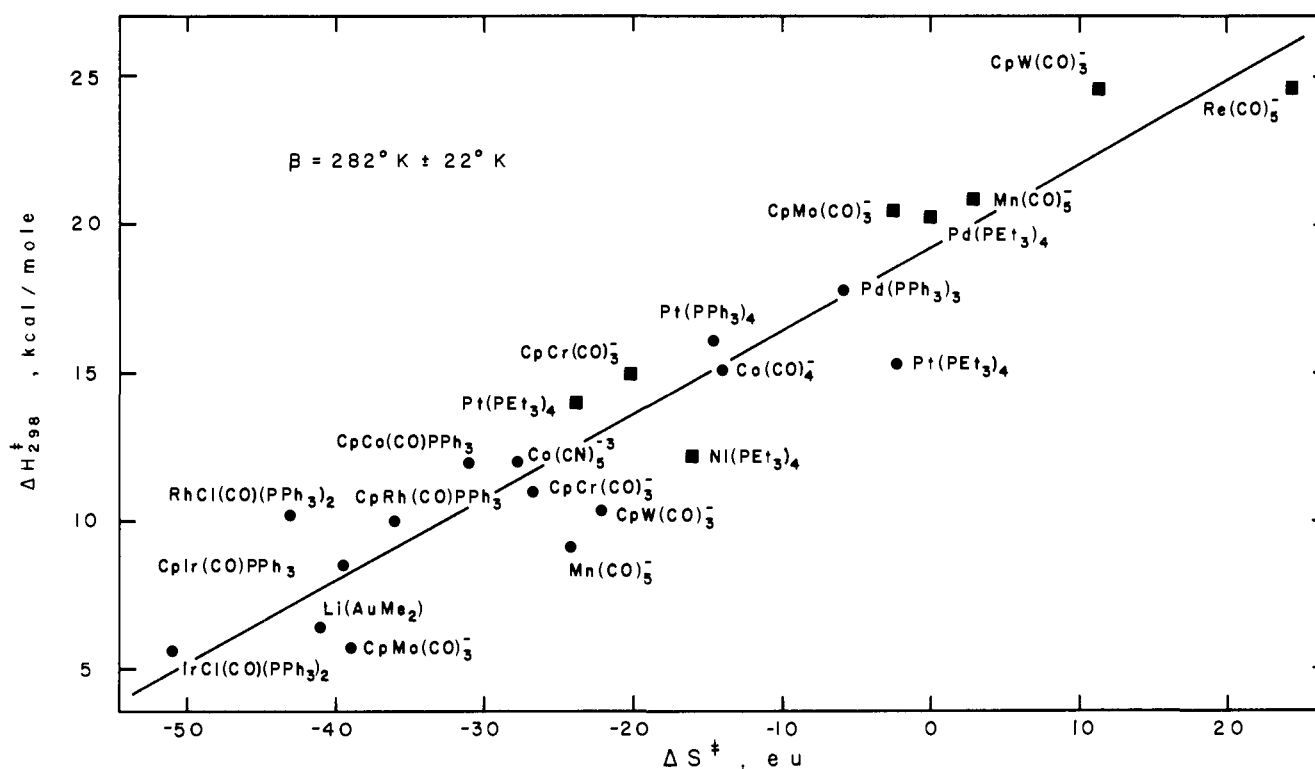


Figure 2. Isokinetic plot for the reaction of transition-metal nucleophiles with MeOTs (O) and MeI (●).

It might also be thought that the use of lithium instead of sodium in the synthesis of these permethylated species favors reaction with MeOTs. However, Table I shows very similar reactivity of $LiMn(CO)_5$ and $NaMn(CO)_5$ toward both MeI and MeOTs. The same result has been found for their reactions with benzyl chloride.⁴⁸

There is no ratio of k_1/k_{OTs} which is as large as the 10^8 – 10^9 found for $Co(CN)_5^{3-}$. The next largest ratio is 10^6 for $Pd(PEt_3)_3$. Studies of this complex by the stereochemical

method led to the conclusion that an S_N2 mechanism was followed with benzylic halide.^{4a} Some racemization was observed and a free-radical component is possible. Evidence for a free-radical mechanism was also found for the reaction with alkyl halides other than methyl.^{50a} $Pt(PEt_3)_3$ is even more prone to free-radical mechanisms.

Reaction with MeOTs could not be observed with $Ni(PPh_3)_3$, $Pd(PPh_3)_3$, and $IrCl(CO)(PPh_3)_2$. In the latter two cases this can be explained by the low reactivity of the com-

plexes even toward MeI. Decomposition of the complex occurred before reaction with MeOTs could be detected. Ni(PPh₃)₃ was also too unstable to detect a slow reaction with MeOTs. Therefore, in these three cases failure to react with MeOTs is not necessarily proof for a free-radical mechanism with MeI. In fact Pd(PPh₃)_{3,4} is known to react with benzyl halides by an S_N2 mechanism.^{4a}

Figure 1 shows a plot of log *k*₁ vs. log *k*_{OTs} for the complexes where both rate constants are known. A number of normal nucleophiles are also included.¹⁴ Except for Li₂Cu₂Me₄ and LiAuMe₂, the other nucleophiles shown a reasonable linear relationship. The compounds 24–28 are neutral complexes studies in benzene. In this solvent the rates with MeOTs are retarded relative to those with MeI.¹⁵ Making allowance for this solvent effect puts 24–28 on the same line as the anionic complexes in THF and the normal nucleophiles (both anionic and neutral) in methanol.

The existence of such a linear free energy relationship usually implies a common mechanism. If the MeOTs reactions are S_N2, it follows that the MeI reaction also must be. However the permethylated species, including Li₂PtMe₄, are not on the lines, even though an S_N2 mechanism is strongly indicated for Li₂Cu₂Me₄.

Another indication of a common mechanism for all systems studied is given in Figure 2. This is a plot of Δ*H*[‡] vs. Δ*S*[‡]. The best straight line gives an isokinetic temperature of 282 ± 22 K.⁵¹ Such a straight line might also be considered evidence for a common S_N2 mechanism. This evidence must be considered doubtful for several reasons. The data refer to several different solvents, for example. Also an isokinetic temperature near room temperature tends to smooth out variations due to experimental error (*T*Δ*S*[‡] = Δ*H*[‡]).⁵² Finally Co(CN)₅³⁻, which reacts by a free-radical mechanism, also lies on the line.

The last observation serves as a warning that free-radical mechanisms, if not the main ones, are nearly competitive with S_N2 mechanisms for many of the complexes in Table III. It also shows that activation parameters by themselves are not evidence for a particular mechanism in oxidative addition.

Acknowledgments. Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society. Thanks are also due to Ma-they-Bishop for the loan of precious metals.

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