direct photolytic substitution of phosphines into $M(CO)_6^-$ (M = Nb, Ta) provides only 35–65% yields of substituted anions. Further, the photolysis procedure must be monitored carefully to prevent decomposition of the products by uv radiation.[7] Finally, the triphenylstannyl derivatives are moderately air stable, are easily handled, and are conveniently stored as sources of substituted anions which may be generated in situ. Effectively, these triphenyltin derivatives are playing the same role as the bis(carbonylmetal)mercury species of other transition metals, which are often much more easily handled than the corresponding metal carbonyl dimers and are readily reduced to carbonyl anions. For example, $Hg(Co(CO)_4)_2$ is a good source of $Co(CO)_4^-$ but is less sensitive to solvents and oxygen than $Co_2(CO)_8$.[10] Corresponding bis(carbonylmetal)mercury species of the group 5 metals are much less thermally stable than triphenylstannyl derivatives. For example, deep red solutions believed to contain $Hg(V(CO)_6)_2$ and/or $HgV(CO)_6Cl$ are obtained by mixing $HgCl_2$ with $[Na(diglyme)_2]V(CO)_6$ in methylene chloride; however, all attempts to isolate this and similar niobium and tantalum species result in decomposition. Substituted carbonyl anions of group 5 metals also give unstable mercury(II) derivatives.[11]

Corresponding triphenylstannylcarbonylvanadium derivatives also undergo clean reduction; however, their direct production from the reaction of $V(CO)_6^-$ and Ph_3SnCl in the presence of the appropriate ligand is a much slower and lower yield reaction than the corresponding niobium and tantalum reactions.[4] For example, $Ph_3SnV(CO)_5Ph_3P$ and $Ph_3SnV(CO)_4$dppe are obtained in 35% and 45% yields, respectively, from $Ph_3SnV(CO)_6$, after reaction periods of 4 days and 1 week, respectively. In contrast, photosubstitution of PPh_3 and dppe into $V(CO)_6^-$ provides substituted anions in greater than 50% yields. A quantitative study of these photopromoted reactions has recently appeared.[12] Because of the low yields in substitution reactions of $Ph_3SnV(CO)_6$, the photolytic route remains the superior method for the production of most substituted vanadium carbonyl anions.[13–15] However, the importance of the triphenylstannyl route to certain of these carbonyl anions was established by preparing $[Et_4N][V(CO)_4(Ph_2PCH_2)_2C(CH_2PPh_2)CH_3]$ which is not available in pure form from the photolysis of $V(CO)_6^-$ and triphos.[16]

A further limitation to the reduction method is that there are certain triphenylstannyl derivatives of substituted vanadium carbonyl anions which can only be prepared from the corresponding anion. Attempts to prepare $Ph_3SnV(CO)_4$diars and $Ph_3SnV(CO)_4$dmpe directly from $Ph_3SnV(CO)_6$ result in the formation of $[V(CO)_3(diars)_2][V(CO)_6]$ and $[Ph_3Sn(dmpe)][V(CO)_6]$, respectively. These products undoubtedly arise from homolytic and heterolytic cleavage of the tin–vanadium bond in $Ph_3SnV(CO)_6$. The latter compound has been shown to be remarkably susceptible to heterolytic cleavage of the Sn–V bond, a process which places a severe constraint on its substitution chemistry. For example, it is completely ionized in donor solvents as weak as THF.[4] We have shown that dmpe reacts quantitatively with both $Ph_3SnV(CO)_6$ and Ph_3SnCl to yield ionic substances of the formula $[Ph_3Sn(dmpe)][V(CO)_6]$ and $[Ph_3Sn(dmpe)]Cl$, where tin is presumably five-coordinate.[16] However, diars is evidently not a sufficiently strong donor to cause significant heterolytic cleavage of $Ph_3SnV(CO)_6$. We believe that the formation of $[V(CO)_3diars][V(CO)_6]$ arises from *homolytic* cleavage of $Ph_3SnV(CO)_6$ in methylene chloride since $V(CO)_6$ interacts with diars to give the same salt.[5] Weakly basic phosphines also appear to interact with $Ph_3SnV(CO)_6$ in this manner, although substitution products are formed in these reactions in varying yields (vide supra).[17,18] Despite the fact that $Ph_3SnV(CO)_4$dmpe and $Ph_3SnV(CO)_4$diars cannot be prepared via the nonphotolytic process described in this paper, these substances have been found in this laboratory to be a convenient and stable form in which to store the $V(CO)_4$dmpe and $V(CO)_4$diars units since the corresponding anions are exceedingly air sensitive. In this sense, we have established the triphenylstannyl unit to be a useful protecting group in organometallic synthesis.

Concluding Remarks

The reduction of various triphenylstannyl derivatives of substituted vanadium, niobium, and tantalum carbonyls by sodium amalgam in tetrahydrofuran provides a useful and often quantitative method for the preparation of corresponding substituted carbonyl anions.

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Registry No. $[Et_4N][V(CO)_4$dppe], 34089-16-2; $Ph_3SnV(CO)_4$triphos, 60479-87-0; $[Et_4N][V(CO)_4$triphos], 60479-89-2; $Ph_3SnV(CO)_4$dppe, 36571-01-4; Ph_3SnCl, 639-58-7; $Na(diglyme)_2[V(CO)_6]$, 15531-13-2.

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(11) J. E. Ellis, unpublished research. Alkylmercury derivatives of $M(CO)_6^-$ and $M(CO)_5PPh_3^-$, however, may be isolated.[4]
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Dynamic Hydrogen-1 Nuclear Magnetic Resonance Line Broadening in Adducts Formed between Transition Metal Complexes and Lanthanide Shift Reagents

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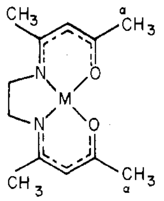
The interaction of lanthanide shift reagents (LSR's) with a nickel(II) compound of type I has recently been reported



I; M = Ni, Pt

by two of us.[2] In addition to the large chemical shifts previously described, the resonance of the α-methyl groups (see structure) undergoes significant changes in line width. As increasing amounts of Eu(fod)$_3$ are added, this resonance first broadens and then narrows. From the concentration dependence of the chemical shift and of the line width, the lifetime of the adduct and the rate constants for its formation and dissociation can be determined. The analysis is a textbook example of the nondilute case of fast-exchange NMR line broadening.

Experimental Section

Nickel(II) and platinum(II) compounds of type I were prepared as previously reported[3] and purified by chromatography on silica gel columns. The Eu(fod)$_3$ was obtained from Pierce Chemical Co. and was dried at 100 °C over P_2O_5 in vacuo for 24 hr before use to yield the anhydrous compound.[4,5] The dried Eu(fod)$_3$ was removed from the drying chamber only in a glovebox filled with dry nitrogen and the successive additions of this LSR to the NMR tube were also carried out in the glovebox. The stoppered sample tube was allowed to equilibrate in the NMR probe for at least 10 min before determination of each spectrum. The $CDCl_3$ was stored over sodium bicarbonate or magnesium foil to remove any HCl present and then dried over Linde 3A molecular sieves before use.[5] Solutions in $CDCl_3$ of the diamagnetic coordination compounds of accurately known concentration ($\sim 10^{-1}$ M) were prepared and the spectra recorded on a Jeol JNM-MH-100 spectrometer (100 MHz) at a probe temperature of 32 °C.

Results and Discussion

The variations in chemical shift and line width for the α-methyl resonance of the nickel(II) compound of type I as increasing amounts of Eu(fod)$_3$ are added are shown in Figure 1. By graphical extrapolation of the α-methyl chemical shifts at $\rho < 0.5$ to $\rho = 1.0$ ($\rho = [\text{Eu}]_{\text{total}}/[\text{Ni}]_{\text{total}}$) a limiting chemical shift of 935 Hz is obtained. By use of this value and the observed chemical shifts, the mole fraction of the nickel(II) compound as the adduct can be calculated directly for each ρ value if a high formation constant for the adduct is assumed (see later).

Since it has been shown that the substrate exchange in lanthanide shift reagent systems is generally a first-order process[5] the lifetime of the nickel compound–LSR adduct can be determined from the observed line widths using the theory appropriate for fast exchange between two sites in the nondilute case[6]

$$\Delta\nu_{1/2} = f_A\Delta\nu_A + f_B\Delta\nu_B + f_A{}^2 f_B\tau_B 2\pi\delta^2 \qquad (1)$$

where $\Delta\nu_{1/2}$ is the half-width of the observed resonance (in Hz) at half-height, $\Delta\nu_A$ is the half-width corresponding to the nickel(II) compound in the absence of adduct formation, $\Delta\nu_B$ is the half-width on complete adduct formation, f_A is the mole fraction of free nickel(II) compound, f_B is the mole fraction of the nickel(II) compound as the LSR adduct, τ_B is the lifetime of the nickel(II) compound–LSR adduct, and δ is the difference between the original chemical shift and the limiting chemical shift on complete adduct formation.

The fast-exchange condition is established by the observation of a single resonance for both the diamagnetic nickel(II) compound and its paramagnetic adduct with the shift reagent.

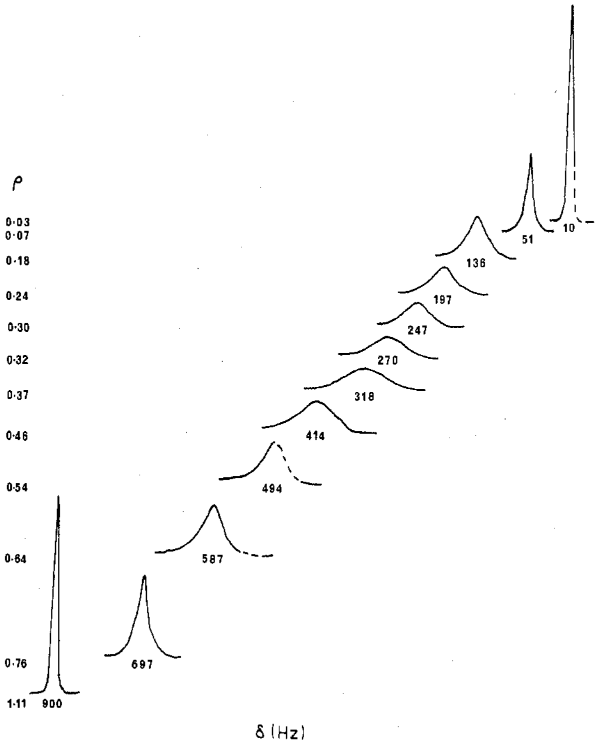


Figure 1. The 100-MHz ^{1}H NMR spectra of the α-methyl group of I (M = Ni) with increasing amounts of Eu(fod)$_3$; $\rho = [\text{Eu}]_{\text{total}}/[\text{Ni}]_{\text{total}}$. The chemical shifts (Hz) relative to the spectrum of the free nickel compound are indicated for each peak.

The half-line-width of the diamagnetic resonance $\Delta\nu_A$ is obtained directly before addition of any shift reagent and the line width $\Delta\nu_B$ of the adduct is obtained from the line width observed at $\rho \simeq 2$ when formation of the adduct is essentially complete. With these values the broadening due to the exchange process is obtained and the lifetime calculated from the final term in (1) using the limiting chemical shift difference between the two sites. A lifetime τ_B of $(1.3 \pm 0.1) \times 10^{-5}$ s is obtained, excluding the last three data points at which $\rho > 1.0$—for these, the exchange broadening is only a small fraction of the line width.

For the exchange process

$$\text{Ni compound} + \text{LSR} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} \text{(Ni compound)–LSR} \qquad (2)$$

this lifetime corresponds to $k_d = \tau_B{}^{-1} = (7.7 \pm 0.6) \times 10^4\ \text{s}^{-1}$. Calculation of the formation rate constant k_f requires knowledge of the equilibrium constant for adduct formation, $K = k_f/k_d$. This can be estimated to be $\sim 1 \times 10^3\ \text{M}^{-1}$ from the chemical shifts observed near $\rho = 1.0$. The inaccuracy of this value arises from the relatively large formation constant and the consequent small degree of dissociation of the adduct. More accurate values could be obtained from more dilute solutions but observation of the NMR signals is difficult under these conditions. Satisfactory agreement with the data is illustrated in Figure 2a where the solid curve is calculated using the values $K = 1000\ \text{M}^{-1}$, $\tau_B = 1.3 \times 10^{-5}$ s, $\Delta\nu_A = 1$ Hz, and $\Delta\nu_B = 2$ Hz. With these values a rate constant for adduct formation, k_f, of $7.7 \times 10^7\ \text{M}^{-1}\ \text{s}^{-1}$ can be calculated.

Similar behavior is observed for the platinum(II) compound, I, for which a slightly larger limiting chemical shift of 1187 Hz is found with a slightly smaller formation constant of $(5 \pm 2) \times 10^2\ \text{M}^{-1}$. From the line-broadening data (Figure 2b) the lifetime of the adduct is found to be $(2.2 \pm 0.2) \times 10^{-5}$ s, with rate constants of $(4.6 \pm 0.4) \times 10^4\ \text{s}^{-1}$ for k_d and $2.3 \times 10^7\ \text{M}^{-1}\ \text{s}^{-1}$ for k_f. These values are thus quite similar to

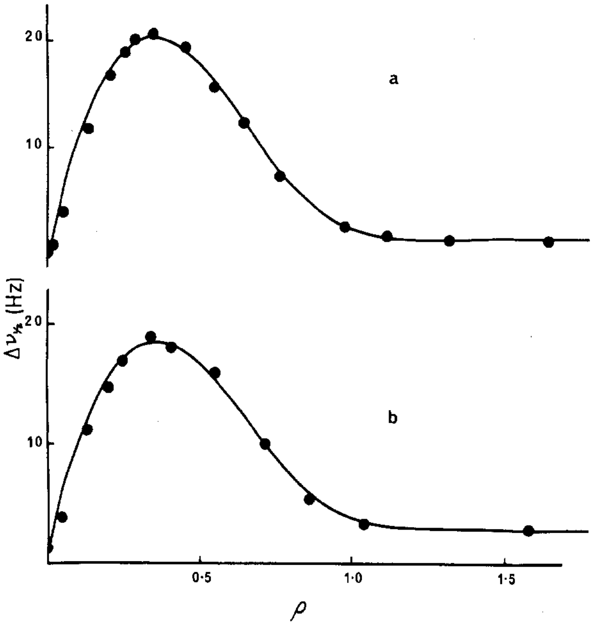


Figure 2. Experimental (●) and calculated (–) half-widths of α-methyl resonance as function of ρ, the $[\text{Eu}]_{\text{total}}/[\text{M}]_{\text{total}}$ ratio: (a) I with M = Ni; (b) I with M = Pt.

those of the nickel(II) compound.

The spectral data observed for these nickel(II) and platinum(II) compounds on formation of lanthanide shift reagent adducts provide classic examples of the nondilute case of two-site fast-exchange NMR line broadening. In each case the appreciable concentrations of both the diamagnetic substrate and its paramagnetic LSR adduct contribute to the last term in eq 1. This term is negligible in the more commonly encountered dilute case typified by the Swift and Connick[7] experiment in which the paramagnetic metal species is present in much lower concentration than the diamagnetic ligand. Differentiation of eq 1 leads to the prediction that, for an infinite formation constant (K), maximum broadening will occur at $\rho = {}^1/_3$—a condition closely approximated by the present systems (Figure 2).

For each complex, broadening of the ⋯CH⋯ ligand proton is also observed. It is clear from the spectra that these proton resonances also reach their maximum broadness near $\rho = {}^1/_3$, but the magnitude of the broadening is small and this, together with the relatively small lanthanide induced shifts, results in these resonances being of little use for calculation of rate data.

A duplicate set of experiments was also performed using Eu(fod)$_3$ and CDCl$_3$ as supplied (without further drying). The results illustrate that the presence of water has a marked effect on the lifetimes of the respective adducts. Under these conditions a lifetime for the nickel adduct of $\sim 5.8 \times 10^{-6}$ s was obtained whereas the value for the corresponding platinum adduct was $\sim 7.0 \times 10^{-6}$ s. Although for a given value of ρ the observed broadening was considerably smaller than for the corresponding anhydrous system, the overall broadening pattern was similar with the observed maximum broadening near to $\rho = {}^1/_3$ in each case.

The magnitude of the observed broadening depends on the mean lifetime of the adduct and on the square of the difference in the chemical shift between the adduct and the free metal complex. In contrast to previous work,[8,9] the dramatic effects found in the present work are a consequence of the longer lifetimes[10] which presumably reflect chelation of the substrate to the LSR as previously discussed.[2]

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Registry No. I (M = Ni), 13878-48-3; I (M = Pt), 16039-95-5; Eu(fod)$_3$, 17631-68-4.

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The Cr^{2+} Reduction of Titanium(IV). Comparisons with the Cr^{2+} Reduction of VO^{2+} and Evidence for a TiO^{2+} Structure in Aqueous Solutions, pH ≤1

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An important consideration when discussing reactions of Ti(IV) in acidic aqueous solutions is the question of the structure of Ti(IV) in such solutions and in particular whether monomeric TiO^{2+} or Ti(OH)$_2{}^{2+}$ (or some other form) is present. As a part of this study on the kinetics and mechanism of the Cr^{2+} reduction of Ti(IV), further attempts have been made to settle this controversial question.[1] A comparison of percentage yields of CrCl^{2+} for the Cr^{2+} reductions of Ti(IV) and V(IV), as well as lack of an [H$^+$] dependence for the Cr^{2+} reduction of Ti(IV) over the range [H$^+$] = 0.1–1.9 M investigated, provides evidence for a TiO^{2+} structure similar to VO^{2+}.

Experimental Section

Reactants. Solutions of Ti(IV) (ca. 0.04 M), V(IV) (ca. 0.20 M), Cr^{2+} (ca. 0.50 M) in dilute perchloric acid (ca. 1 M), and LiClO$_4$ were prepared by procedures as used in other work from these laboratories.[2] Solutions of HClO$_4$ and HCl were obtained by dilution of concentrated Analar acids. Air-free techniques (N$_2$ gas), Atlas nylon syringes, rubber serum caps, and stainless steel needles were used.

Stoichiometry. Spectra of reactant solutions (a) [Cr^{2+}] = 0.05 M, [Ti(IV)] = 0.10 M and (b) [Cr^{2+}] = 0.136 M, [Ti(IV)] = 0.013 M, both with [H$^+$] = 0.50 M, were measured at 350–750 nm after ca. 1 min reaction time. Analysis of these indicated a reaction as in (1), with a stoichiometry 1.00 ± 0.02. No evidence was obtained for

$$\text{Cr(II)} + \text{Ti(IV)} \rightarrow \text{Cr(III)} + \text{Ti(III)} \tag{1}$$

absorbing species other than monomers in (1), peak positions for Cr^{2+} (λ 715 nm, ϵ 4.8 M^{-1} cm^{-1}), Ti^{3+}(λ 502, ϵ 3.97), and Cr^{3+} (λ 408, ϵ 15.5; λ 571, ϵ 13.2). Slower subsequent reactions occur due to the Ti(III) reduction of perchlorate[3] and, if Cr^{2+} is present in excess, reduction of the Ti(IV) which is regenerated.

Kinetics. Formation of Cr^{3+} was monitored on a Durrum-Gibson stopped-flow spectrophotometer at λ 408 nm. At this Cr^{3+} peak position ϵ 0.8 M^{-1} cm^{-1} for Ti^{3+}. Runs monitored at 502 and 575 nm were in good agreement with those at 408 nm. The Cr^{2+} reactant was generally in tenfold excess. First-order plots of absorbance (A) readings log ($A_\infty - A_t$) against time (where A_∞ is the observed final