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Kinetics and Mechanisms of Ligand Substitution Reactions of the Vanadium Triad Metals. Syntheses and Reactivities of $(\eta^5\text{-}C_5H_5)M(CO)_3(C_4H_8E)$ (M = Nb, E = S, Se, Te; M = Ta, E = S)

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Kinetic studies were performed for CO substitution reactions of $CpM(CO)_4$ (M = Nb, Ta) and for dialkylchalcogenide substitution reactions of $CpM(CO)_3(C_4H_8E)$ (M = V, E = S; M = Nb, E = O, S, Se, Te; M = Ta, E = O, S) with phosphines. The syntheses and characterization of the new compounds $CpM(CO)_3(C_4H_8E)$ (M = Nb, E = S, Se, Te; M = Ta, E = S) are reported. Both $CpM(CO)_4$ and $CpM(CO)_3(C_4H_8E)$ were found to react by the same mechanism. For M = V, a dissociative mechanism was observed, while for M = Nb, Ta both dissociative and associative mechanisms were observed. This change in mechanism is attributed to the larger size of the Nb and Ta centers. The reactivity of the compounds was found to increase in the order V > Nb > Ta. The higher reactivity of the V compounds compared to the Nb compounds is unusual when compared to other triads, where the second-row metal usually forms the most reactive compound. The reactivity of the $CpM(CO)_3(C_4H_8E)$ compounds was found to increase in the order Te < Se < S < O, indicating that the heavier chalcogenides form more stable complexes than the higher chalcogenides.

Introduction

Many kinetic studies on ligand exchange in metal carbonyl compounds have been carried out over the years.[1] Some of these studies have focused upon the reactions of isostructural metal carbonyl complexes within the same triad in order to determine the effect of the metal center on reaction rates and mechanisms. The results of these studies has led to the formation of the "triad rule", which states that for mononuclear organometallic complexes of a triad, the complex containing the second-row transition metal will react at the fastest rate. Generally the first-row metal complex reacts at the second fastest rate, while the third-row metal complex reacts at the slowest rate. This rule has been shown to hold for the triads of groups 4 (Ti),[2] 6 (Cr),[3] 8 (Fe),[4] 9 (Co),[5] and 10 (Ni).[6] To date, no study of the group 5 triad (V, Nb, Ta) has been reported.

Kinetic studies on the group 5 compounds $CpV(CO)_4$[7] and $InV(CO)_4$[8] (Cp = C_5H_5, In = indenyl, C_9H_7) show that both of these compounds react with phosphines to form monosubstituted complexes by a dissociative (S_N1) mechanism. Thioether vanadium carbonyl compounds suitable for kinetic studies have also been reported. They include the compounds $CpV(CO)_3(C_4H_8S)$[9] and $CpV(CO)_3(SMe_2)$.[10] The thioether ligands in both complexes are substitution labile and can readily be replaced by phosphines or pyrrolidine (for the C_4H_8S complex) or by CO, $SeMe_2$, and $TeMe_2$ (for the SMe_2 complexes). Equilibria studies[11] for the $CpV(CO)_3(EMe_2)$ series showed that the stability of the complex increased in the order S < Se < Te. This trend, when viewed in light of the known instability of $CpV(CO)_3THF$ (THF = C_4H_8O) (decomposes > −20 °C)[11] is somewhat surprising since the early transition metals are generally considered to be oxophilic. In addition, thioethers are both poor σ donors and poor π acceptors,[12] suggesting the ether complexes should be more stable than the thioether complexes.

The primary goal of this work was to complete the kinetic studies of the group 5 triad by using the compounds $CpM(CO)_4$ (M = Nb, Ta). However, due to the high temperatures required to observe the reactions of $CpTa(CO)_4$ with phosphines, another series of group 5 compounds containing a more labile ligand was desired for study. Eventually, the series $CpM(CO)_3$tht (tht = tetrahydrothiophene, C_4H_8S) was prepared, and the replacement of the labile tht ligand by phosphines was studied. The secondary goal of this work was to study the effect of changing the donor atom E of the ligand C_4H_8E (E = O, S, Se, Te) on the reactivity of $CpNb(CO)_3(C_4H_8E)$. Niobium rather than vanadium was chosen as the central metal because $CpNb(CO)_3THF$ can be handled at ambient temperatures[13] whereas $CpV(CO)_3THF$ decomposes at ambient temperatures. This study provides more information on the relative metal–ligand bond strengths of ethers, thioethers, and the less common seleno- and telluroethers.

Experimental Section

General Procedures. The cyclopentadienyl metal carbonyl derivatives of the group 5 metals used in this work are all air-

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sensitive compounds. All manipulations of these compounds were carried out under an atmosphere of N_2, using standard Schlenk techniques or a N_2-filled glovebox. Toluene, decalin, hexadecane, pentane, and tetrahydrofuran were predried and distilled from Na or Na/benzophenone before use. Dichloromethane was dried and distilled from P_2O_5 under a N_2 atmosphere before use. The $CpV(CO)_4$ was purchased from Strem and purified by sublimation before use. The compounds $CpM(CO)_4$ (M = Nb, Ta),[14] $CpV(CO)_3$tht,[9] C_4H_8Se,[15] and C_4H_8Te[16] were prepared according to literature methods. Unstable $CpNb(CO)_3$THF and $CpTa(CO)_3$THF were prepared by photolysis and were used in situ.[13] Tetrahydrothiophene and all phosphines were purchased and purified by appropriate methods before use.

All the chalcogenide complexes $CpM(CO)_3(C_4H_8E)$ were prepared by the photolysis of $CpM(CO)_4$ in THF in the presence of excess C_4H_8E (eq 1). The solvent plays an important role in these

$$CpM(CO)_4 + C_4H_8E \xrightarrow{h\nu} CpM(CO)_3(C_4H_8E) + CO \quad (1)$$

$$M = Nb, E = O, S, Se, Te; M = Ta, E = O, S$$

reactions. The use of either toluene or heptane for M = Nb or Ta leads to substantial decomposition and very low yields of product, while the use of THF allows for reasonable yields of product. This difference is attributed to the stabilization by THF of the highly reactive "$CpM(CO)_3$" intermediate initially formed to give $CpM(CO)_3$THF. $CpM(CO)_3$THF then reacts with C_4H_8E to give the desired product.

(Cyclopentadienyl)tricarbonyl(tetrahydrothiophene)niobium(I), $(C_5H_5)Nb(CO)_3(C_4H_8S)$. This compound was synthesized by a procedure similar to those used for $CpV(CO)_3$tht and $CpV(CO)_3(SMe_2)$. A 0.30-g (1.1 mmol) sample of $CpNb(CO)_4$ was dissolved in 20 mL of THF in a borosilicate glass Schlenk tube. Excess (ca. 5 equiv) tetrahydrothiophene was added, and the resulting orange solution was exposed to UV light from a 15-W fluorescent black light blulb for approximately 8 h. The flask was periodically connected to vacuum line to remove any CO gas. The progress of the reaction was monitored by IR. When the photolysis was mostly complete, the resulting dark red solution was filtered (frit/celite) and concentrated to ca. 1 mL. The addition of 15 mL of pentane caused the product to crystallize at ambient temperature as dark red needles. The product was isolated, washed with 2 × 7 mL of cold pentane, and dried under vacuum. The product was purified by recrystallization from toluene/pentane. Yield 0.29 g (80%) of dark purple–red crystals; mp 85–86 °C (dec). IR (Nujol mull): 1951 (s) , 1852 (s), 1830 (s), 1808 (s), 1442 (m), 1309 (m), 1267 (m), 1254 (m), 1206 (w), 1193 (w), 1131 (w), 1111 (w), 1061 (m), 1010 (w), 1005 (m), 957 (w), 887 (w), 882 (m), 801 (s), 671 (w) cm^{-1}. ^1H NMR (benzene-d_6): δ 5.06 (s, 5 H, Cp); 2.23 (m, 4 H, tht), 1.12 (m, 4 H, tht). ^{13}C NMR (benzene-d_6): δ 95.02 (Cp), 43.67 (tht), 30.30 (tht). UV (toluene): λ_{max} 529 nm; $\epsilon = 440\ cm^{-1}\ M^{-1}$. Mass spectrum: *m/e* (relative intensity) 330 (19), 272 (25), 243 (15), 242 (100), 216 (12), 190 (64), 164 (17), 158 (25), 121 (13), 88 (36), 87 (13), 60 (49), 59 (11), 47 (13), 46 (14), 45 (15).

(Cyclopentadienyl)tricarbonyl(tetrahydrothiophene)tantalum(I), $(C_5H_5)Ta(CO)_3(C_4H_8S)$. This compound was prepared according to the same procedure as $(C_5H_5)Nb(CO)_3$tht. Yield 57% dark purple–red crystals; mp 112–114 °C (dec). IR (Nujol mull): 3941 (w), 3883 (w), 3741 (w), 3653 (w), 3598 (w), 3111 (w), 1944 (s), 1842 (s), 1821 (sh), 1794 (s), 1423 (m), 1441 (m), 1354 (w), 1327 (w), 1309 (m), 1267 (m), 1253 (m), 1206 (mw), 1193 (m), 1131 (m), 1111 (w), 1062 (m), 1036 (w), 1010 (m), 1004 (m), 957 (mw), 887 (mw), 882 (m), 808 (s), 669 (w) cm^{-1}. ^1H NMR (benzene-d_6): δ 5.02 (s, 5 H, Cp); 2.29 (m, 4 H, tht); 1.11 (m, 4 H, tht). ^{13}C NMR (benzene-d_6): δ 94.0 (Cp); 45.25 (tht), 30.33 (tht). UV (toluene): λ_{max} at 514 nm; $\epsilon = 510\ cm^{-1}\ M^{-1}$. Mass spectrum: *m/e* (relative intensity) 419 (10), 418 (52), 362 (24), 360 (44), 334 (12), 333 (15), 332 (92), 331 (16), 330 (85), 306 (20), 304 (61), 303 (13), 302 (10), 279 (16), 278 (100), 277 (12), 276 (10), 252 (32), 251 (18), 250 (12), 246 (10), 238 (10), 165 (19), 88 (12), 60 (16).

(Cyclopentadienyl)tricarbonyl(tetrahydroselenophane)niobium(I), $(C_5H_5)Nb(CO)_3(C_4H_8Se)$. $CpNb(CO)_3$thse (thse = tetrahydroselenophene) was isolated as dark red crystals. Yield 50%; mp 83–84 °C. IR (Nujol mull): 1946 (s), 1851 (vs), 1828 (s), 1807 (s), 1434 (m), 1310 (m), 1250 (m), 1254 (m), 1196 (m), 1116 (w), 1059 (w), 1041 (w), 1011 (m), 1004 (m), 982 (w), 953 (m), 855 (m), 800 (ms) cm^{-1}. ^1H NMR (benzene-d_6): δ 5.05 (s, 5 H, Cp); 2.43 (s, 4 H, thse); 1.22 (s, 4 H, thse). ^{13}C NMR (benzene-d_6): δ 94.59 (s, Cp); 36.45 (s, thse); 32.27 (s, thse). UV (toluene): λ_{max} 523 nm; $\epsilon = 450\ mol^{-1}\ cm^{-1}$. Mass spectrum: *m/e* (relative intensity) 380 (14), 378 (61), 376 (34), 375 (13), 374 (13), 350 (32), 348 (16), 322 (26), 320 (43), 318 (23), 294 (30), 293 (14), 292 (100), 291 (16), 290 (99), 289 (25), 288 (52), 287 (13), 286 (16), 270 (14), 266 (10), 264 (18), 242 (17), 240 (14), 238 (67), 236 (37), 235 (13), 234 (15), 214 (22), 186 (13), 158 (39), 136 (40), 134 (23), 55 (49).

(Cyclopentadienyl)tricarbonyl(tetrahydrotellurophane)niobium(I), $(C_5H_5)Nb(CO)_3(C_4H_8Te)$. $CpNb(CO)_3$thte (thte = tetrahydrotellurophene) was isolated as red crystals. Yield 53%; mp 60–61 °C. IR (Nujol mull): 1957 (s), 1873 (m), 1852 (s), 1455 (m), 1419 (m), 1310 (w), 1262 (w), 1243 (m), 1236 (m), 1187 (m), 1134 (w), 1110 (w), 1060 (w), 1042 (w), 1023 (2), 1008 (m), 952 (w), 838 (w), 829 (w), 810 (m), 795 (m), 759 (w) cm^{-1}. ^1H NMR (benzene-d_6): δ 5.01 (s, 5 H, Cp); 2.84 (m, 2 H, thte); 2.64 (m, 2 H, thte); 1.27 (m, 2 H, thte); 1.11 (m, 2 H, thte). ^{13}C NMR (benzene-d_6): δ 93.83 (d, $J_{C\text{-}Te}$ = 29.7 Hz, Cp), 34.21 (s, thte), 15.04 (s, thte). UV (toluene): λ_{max} 488; $\epsilon = 630\ cm^{-1}\ M^{-1}$. Mass spectrum: *m/e* (relative intensity) 428 (34), 426 (32), 424 (21), 400 (3), 372 (8), 344 (22), 342 (70), 341 (12), 340 (79), 339 (14), 338 (58), 337 (19), 336 (28), 334 (10), 316 (23), 314 (31), 312 (23), 289 (11), 288 (100), 287 (13), 286 (95), 284 (64), 283 (31), 282 (21), 280 (11), 262 (14), 260 (18), 258 (12), 186 (17), 184 (11), 170 (14), 169 (13), 158 (81), 156 (12), 132 (12), 131 (10), 130 (17), 55 (34).

(Cyclopentadienyl)tricarbonyl(dimethylphenylphosphine)tantalum(I), $(C_5H_5)Ta(CO)_3P(CH_3)_2C_6H_5$. A 0.15-g (0.36 mmol) sample of $CpTa(CO)_3$tht and 1.5 equiv of PMe_2Ph were dissolved in 15 mL of toluene. The dark red solution was then heated to 100 °C for 1 h. The resulting orange solution was filtered (frit/celite) and concentrated to ca. 1 mL. Fifteen milliliters of pentane was added and the solution cooled to −30 °C. The product formed orange crystals that were isolated, washed with 10 mL of cold pentane, and dried under vacuum. Yield 0.11 g (66%); mp 110–111 °C. IR (Nujol mull): 1956 (sh), 1939 (s), 1838 (vs), 1823 (vs), 1809 (s), 1581 (w), 1465 (s), 1436 (m), 1420 (m), 1409 (w), 1343 (w), 1325 (w), 1305 (w), 1287 (m), 1195 (w), 1187 (w), 1159 (w), 1106 (w), 1095 (m), 1073 (w), 1059 (w), 1030 (w), 1011 (m), 1005 (m), 944 (m), 910 (m), 901 (m), 831 (m), 813 (m), 802 (m), 742 (m), 734 (w), 722 (m), 710 (w), 705 (w), 692 (m), 678 (m) cm^{-1}. IR (toluene): 1950 (ms), 1858 (m), 1832 (s) cm^{-1}. ^1H NMR (benzene-d_6): δ 7.28–7.21 (m, 2 H); 7.05–7.02 (m, 3 H); 4.84 (s, 5 H, Cp), 1.36 (d, J_{PH} = 8.1 Hz, 6 H, CH_3). ^{13}C NMR (benzene-d_6): δ 258.23 (s, CO), 140.75 (d, $J_{P\text{-}C}$ = 37.0 Hz); 130.15 (s); 93.98 (s, Cp), 20.41 (d, J_{PC} = 30.9 Hz, CH_3), remaining phenyl carbons were obscured by the solvent.

(Cyclopentadienyl)tricarbonyl(triphenyl phosphite)tantalum(I), $(C_5H_5)Ta(CO)_3P(OC_6H_5)_3$. This compound was prepared by the same method used to prepare $CpTa(CO)_3PMe_2Ph$ and was isolated as yellow needles. Yield 82%: mp 151–152 °C. IR (Nujol mull): 3811 (w), 1965 (s), 1877 (s), 1862 (vs), 1590 (m), 1490 (m), 1423 (m), 1308 (w), 1261 (w), 1223 (w), 1191 (m), 1163 (m), 1073 (mw), 1024 (mw), 1013 (w), 1007 (w), 981 (w), 920 (m), 908 (m), 890 (m), 841 (w), 822 (mw), 813 (mw), 764 (m), 731 (m), 723 (m), 693 (m), 614 (w) cm^{-1}. IR (toluene): 1973 (ms), ~1884 (sh), 1868 (s) cm^{-1}. ^1H NMR (benzene-d_6): δ 7.33 (d, J_{HH} = 8.1 Hz, 2 H), 7.04 (t, J_{HH} = 8.0 Hz); 6.88 (t, J_{HH} = 7.5 Hz); 4.73 (s, 5 H, Cp). ^{13}C NMR (benzene-d_6): δ 152.38 (d, J_{PC} = 7.3 Hz); 130.30 (s); 125.69 (s); 122.68 (d, J_{PC} = 4.4 Hz), 93.56 (s, Cp). Anal. Calcd for $C_{26}H_{20}O_3PTa$: C, 48.77; H, 3.15. Found: C, 48.28; H, 2.61.

(Cyclopentadienyl)tricarbonyl(tri-*n*-butylphosphine)tantalum(I), $(C_5H_5)Ta(CO)_3(n\text{-}C_4H_9)_3P$. This compound was isolated from the kinetic experiments by column chromatography. The remaining solution from the kinetic experiments of $CpTa(CO)_4$ and $CpTa(CO)_3$tht with P(*n*-Bu)$_3$ were combined and the toluene removed under vacuum. The remaining orange solution

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was chromatographed through a silica column, using hexanes to wash the excess hexadecane and P(n-Bu)$_3$ through the column and then toluene to remove the product. A second run through a silica column (same conditions) was performed to completely clean the product. The collected product was then recrystallized from toluene/pentane at −78 °C and isolated as orange crystals, mp 110–111 °C. IR (Nujol mull): 3875 (w), 3756 (w), 3638 (w), 3112 (w), 1938 (s), 1840 (vs), 1457 (m), 1425 (mw), 1414 (mw), 1357 (w), 1306 (w), 1278 (w), 1213 (w), 1097 (mw), 1057 (mw), 1013 (mw), 1005 (w), 907 (mw), 826 (mw), 806 (m), 783 (mw), 730 (mw) cm^{-1}. IR (toluene): 1949 (ms), 1854 (m), 1834 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.45 (s, 5 H, Cp); 1.71 (m, 6 H, PBu$_3$); 1.40, 1.36 (overlapping m, 12 H, PBu$_3$); 0.95 (t, J_H = 7.2 Hz, 9 H, PBu$_3$). ^{13}C NMR (CDCl$_3$): δ 260.0 (s, CO), 258.33 (d, J_{PC} = 26 Hz, CO), 92.74 (s, Cp), 29.45 (d, $J_{P\text{-}C}$ = 24 Hz, PBu$_3$), 28.21 (s, PBu$_3$), 24.18 (d, J_{PC} = 13 Hz, PBu$_3$), 13.74 (s, PBu$_3$). Anal. Calcd for $C_{20}H_{32}O_3PTa$: C, 45.12; H, 6.06. Found: C, 44.86; H, 5.79.

Instrumentation. The infrared spectra were obtained on a Nicolet 5PC FT-IR spectrometer using either a cell with 0.2-mm KBr windows or, in the case of CpV(CO)$_3$tht, a special P/N 20.500 variable-temperature IR cell with 0.5-mm AgCl windows. The visible spectra were obtained on a Varian Cary 219 spectrophotometer using 1-cm quartz cells designed for use with air-sensitive solutions. The spectrophotometer was equipped with a heating/cooling jacket around the sample chamber to permit the use of various temperatures for kinetic experiments. The temperature baths used were either a Neslab RTE-8 refrigeration circulating bath (for temperatures below 30 °C) or a Hacke FJ type temperature bath (for temperatures above 30 °C but below 120 °C). A special bath was constructed for use at high temperatures (up to 215 °C). The bath consisted of a 1000-mL beaker wrapped with a heating tape and then surrounded by glass wool. The bath was filled with silicon oil, and the temperature was regulated by a Cole-Parmer Digi-Sense temperature controller with a type J thermocouple. This system was able to maintain temperatures within ±0.2 °C.

The NMR spectra were obtained on either a Varian XL400 spectrometer or a JOEL FX-270 spectrometer. Mass spectra were obtained on a HP5985A spectrometer. Both of these instruments were operated by personnel of the Northwestern Analytical Services Laboratory. Melting points were obtained from samples sealed in capillary tubes on a Mel-Temp apparatus. Elemental analyses were performed by Oneida Research Services.

Kinetic Studies. All kinetic experiments were run under pseudo-first-order conditions (at least a 10-fold excess of PR$_3$). The following conditions were used during the kinetic studies of the various metal carbonyl compounds.

CpM(CO)$_4$ (M = Nb, Ta). Approximately 5 mg of CpM(CO)$_4$ in hexadecane was used for each kinetic run. Ligand solutions (4.7 mL) were equilibrated in a constant-temperature bath, and then the metal complex in hexadecane was added (0.3 mL). The reaction rate was then monitored by IR by periodically removing 0.2-mL aliquots of the reaction mixture and injecting the samples into an IR cell that had been purged with N$_2$.

CpV(CO)$_3$tht. Approximately 8 mg of CpV(CO)$_3$tht in toluene was used for each kinetic rung. Solutions of the ligand and of the metal complex in toluene were equilibrated in a temperature bath. The solutions were then rapidly mixed together and 1.0 mL of the resulting solution was transferred to the thermostated VT-IR cell. The reaction rate was then monitored by periodically collecting IR spectra.

CpM(CO)$_3$(C$_4$H$_8$E) (M = V, E = S; M = Nb, E = S, Se, Te; M = Ta, E = S). Approximately 2–3 mg of the metal complex was used in each kinetic run. The solvent was toluene for all the complexes except CpNb(CO)$_3$(C$_4$H$_8$Te), where the temperatures needed for reaction required the use of decalin. CpTa(CO)$_3$THF was prepared by photolysis of CpTa(CO)$_4$ in THF. The THF was removed in vacuo, and the resulting green residue was immediately dissolved in toluene and added to the ligand solution. The ligand solutions (2.8 mL) were equilibrated in the sample cells while in the sample chamber of the spectrophotometer. The metal complex was then added (in 0.2 mL of solvent), and the reaction rate was monitored by periodically recording the absorbance at a wavelength close to the peak maximum of the starting metal carbonyl. The wavelengths used were M = V, E = S, 523 nm; M = Nb, E = S, 530 nm; M = Nb, E = Se, 525 nm; M = Nb, E = Te, 500 nm; M = Ta, E = O, 595 nm; and M = Ta, E = S, 515 nm.

CpNb(CO)$_3$THF. This compund was too unstable to isolate as a solid and was used in situ instead. For each run, the CpNb(CO)$_3$THF used was prepared by the photolysis of approximately 2 mg of CpNb(CO)$_4$ in THF using a 15-W fluorescent black light bulb. For the phosphine concentration studies, the CpNb(CO)$_3$THF solution (2.7 mL) was equilibrated in the sample chamber of the spectrophotometer. The ligand solution in dichloromethane (0.3 mL) was then added. For the THF concentration study, the ligand solution of THF in dichloromethane (2.7 mL) was equilibrated in the sample chamber, and then the metal complex in 0.3 mL of THF was added. For both studies, the rate of reaction was monitored by periodically recording the absorbance of the starting metal carbonyl at 605 nm.

The rate constants were determined by measuring either the decrease of one of the carbonyl bands or the decrease of the visible absorbance of the starting metal carbonyl. Plots of ln A versus t for the IR studies were linear for at least 2.5–3.0 half-lives, while plots of ln $(A - A_\infty)$ versus t for the UV–visible studies were linear for at least 2 half-lives. The k_{obsd} values were obtained from the slope of these lines as determined by the least-squares method and were reproducible to within ±5%. Correlations of the lines were very good ($r^2 > 0.999$).

The second-order rate constants, k_2, were obtained from the slope of the lines calculated by the least-squares method for plots of k_{obsd} versus concentration of ligand, while first-order rate constants, k_1, were obtained from the intercept of the same lines with the k_{obsd} axis. In cases where the metal complex did not exhibit second-order behavior, the first-order rate constants were obtained directly from the average values of k_{obsd} for reactions at the same temperature. Activation parameters ΔH^* and ΔS^* were calculated by the least-squares method from a plot of ln (k/T) versus $1/T$ where T is the temperature and k is either a first- or second-order rate constant. Correlations of the activation parameter least-squares lines were very good ($r^2 > 0.995$) for all reactions.

Results

CpM(CO)$_4$ (M = Nb, Ta). The reactions of CpM(CO)$_4$ with phosphines in hexadecane proceeded according to eq 2 to give the monosubstituted products CpM(CO)$_3$L.

$$\mathrm{CpM(CO)_4 + PR_3 \rightarrow CpM(CO)_3PR_3 + CO} \qquad (2)$$

$$\mathrm{M = Nb, Ta;\ PR_3 = P(}n\mathrm{\text{-}Bu)_3,\ P(OPh)_3,\ PMe_2Ph}$$

Small amounts of the disubstituted products CpM(CO)$_2$(PR$_3$)$_2$ were also observed to form from the monosubstituted products during the course of the reaction. For M = Nb, the substitution products are known compounds and hence were not isolated, but were identified by their IR spectra.[17] For M = Ta, the product CpTa(CO)$_3$PBu$_3$ was isolated from the kinetic reactions, while CpTa(CO)$_3$P(OPh)$_3$ and CpTa(CO)$_3$PMe$_2$Ph were prepared from CpTa(CO)$_3$tht and the appropriate phosphine. All three Ta products were characterized by ^{1}H and ^{13}C NMR spectroscopies and showed the expected 3 CO bands in the solution IR spectra. Despite the high temperatures used in the Ta study, no decomposition of the organometallic compounds was observed.

Values of k_{obsd} were obtained by monitoring the decrease of the carbonyl bands of the starting metal carbonyl. A representative example of the IR spectra recorded during the kinetic reactions is shown in Figure 1. Values of k_{obsd} obtained in aluminum foil lined flasks were essentially the same as those obtained when the solutions were exposed to ambient light, indicating that no significant photoreactions were occurring during data collection. Plots of k_{obsd} versus ligand concentration were found to show first-order dependence upon the concentration of entering nucleophile; however, plots of k_{obsd} versus ligand concen-

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[17] (a) Bechthold, H.-C.; Rehder, D. *J. Organomet. Chem.* **1981**, *206*, 305. (b) Bechthold, H.-C.; Rehder, D. *Z. Naturforsch.* **1984**, *39b*, 323.

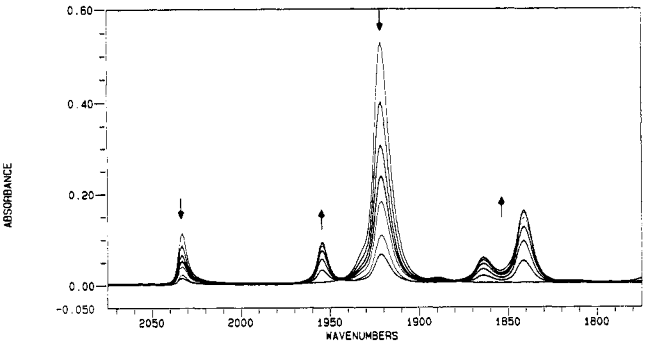


Figure 1. Infrared spectral changes for the reaction between $CpTa(CO)_4$ and $P(n\text{-}Bu)_3$ in hexadecane at 195 °C.

Table I. First- (k_1) and Second-Order (k_2) Rate Constants for the Reactions of $CpM(CO)_4$ with Phosphines (Eq 2) in Hexadecane

temp, °C	M	L	10^4k_1, s^{-1}	10^4k_2, s^{-1} M^{-1}
109.5	V[a]	$P(n\text{-}Bu)_3$	0.786	
119.3	V[a]	$P(n\text{-}Bu)_3$	2.54	
129.5	V[a]	$P(n\text{-}Bu)_3$	8.31	
150.0	Nb	$P(n\text{-}Bu)_3$	1.25	0.728
150.0	Nb	PMe_2Ph	1.16	2.08
160.0	Nb	$P(OPh)_3$	3.82	<0.1
160.0	Nb	$P(n\text{-}Bu)_3$	3.80	1.49
160.0	Nb	PMe_2Ph	3.62	4.09
170.0	Nb	$P(n\text{-}Bu)_3$	11.1	2.67
170.0	Nb	PMe_2Ph	10.6	8.12
195.0	Ta	$P(n\text{-}Bu)_3$	1.20	0.37
205.0	Ta	$P(n\text{-}Bu)_3$	3.44	0.60
215.0	Ta	$P(n\text{-}Bu)_3$	9.31	1.05

[a] Average value of k_{obsd} from ref 7.

Table II. Kinetic Parameters for Substitution Reactions (Eq 2) of $CpM(CO)_4$

M	$\Delta H_1^\ddagger$, kcal/mol	$\Delta S_1^\ddagger$, esu	L	$\Delta H_2^\ddagger$, kcal/mol	$\Delta S_2^\ddagger$, esu
V[a]	35.3 ± 0.5	14.6 ± 1.2			
Nb	40.1 ± 0.9	17.6 ± 2.1	$P(n\text{-}Bu)_3$	23.5 ± 2.9	-22.5 ± 6.7
	40.6 ± 1.1	18.8 ± 2.4	PMe_2Ph	24.7 ± 1.3	-17.8 ± 3.0
Ta	45.8 ± 0.8	20.5 ± 1.5	$P(n\text{-}Bu)_3$	23	-31

[a] Reference 7.

tration for various phosphines at the same temperature gave similar, non-zero intercepts (Figure 2). Thus, the reactions of $CpM(CO)_4$ (M = Nb, Ta) occur by simultaneous dissociative (k_1) and associative (k_2) pathways. The plots of k_{obsd} versus ligand concentration fit eq 3. The

$$k_{obsd} = k_1 + k_2[PR_3] \qquad (3)$$

first- and second-order rate constants obtained from these plots are summarized in Table I. The results for $CpV(CO)_4$,[7] which was found by other workers to react only by a dissociative mechanism, are included for comparison. Activation parameters for the associative and dissociative reactions are summarized in Table II. Due to the small values of k_2 observed for $CpTa(CO)_4$, accurate values of $\Delta H_2^\ddagger$ and $\Delta S_2^\ddagger$ could not be obtained. The values given in Table II for the associative reaction of $CpTa(CO)_4$ are estimates.

Chalcogenide Complexes. The chalcogenide complexes $CpM(CO)_3(C_4H_8E)$ (M = V, E = S; M = Nb, E = O, S, Se, Te; M = Ta, E = O, S) were readily prepared by the photolysis reaction of the appropriate metal carbonyl with the desired ligand (eq 1). Some spectroscopic data for the complexes are given in Table III. The products were isolated as solids (except for $CpNb(CO)_3THF$ and $CpTa(CO)_3THF$) and were stored under nitrogen. All of the products were air sensitive in the solid state and formed very air-sensitive solutions. It was also noted that the more labile complexes (M = V, E = S; M = Nb, E = S, O) tended to decompose in solution to $CpM(CO)_4$ over the course of several hours if excess ligand was not present. The $CpNb(CO)_3THF$ was so labile that the complex would slowly decompose (over 12 h) at room temperature even in neat THF. The more stable systems showed much less decomposition in solution. This trend was also noted in the mass spectra of the $CpNb(CO)_3(C_4H_8E)$ compounds, where E = S, Se, or Te. The mass spectra for these compounds showed that significant amounts of $CpNb(CO)_4$ formed in the sample chamber when E = S, much less $CpNb(CO)_4$ was observed when E = Se, and virtually no $CpNb(CO)_4$ was observed when E = Te.

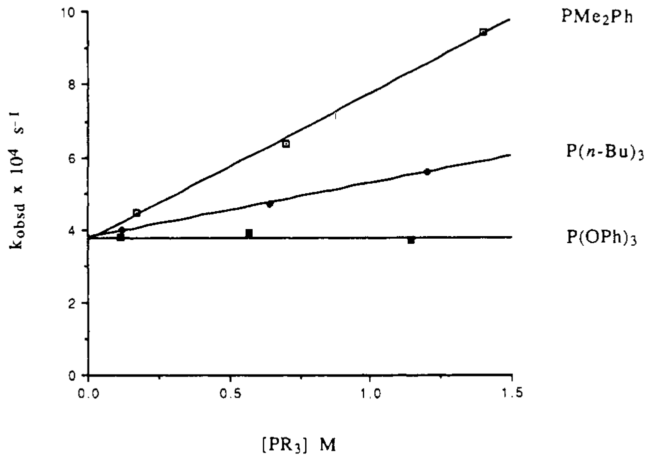


Figure 2. Plot of k_{obsd} versus PR_3 concentration for the reaction of $CpNb(CO)_4$ with PMe_2Ph, $P(n\text{-}Bu)_3$, and $P(OPh)_3$ in hexadecane at 160 °C.

Table III. UV and IR Data for the Compounds $CpM(CO)_3(C_4H_8E)$

M	E	color	λ_{max}[a]	IR
V	S	dark red	523	1957 (m), 1856 (s) THF 1962 (ms), 1875 (m) 1859 (s) decalin
Nb	O	green	603[b]	1958 (m), 1837 (s) THF
	S	dark red	529	1960 (m), 1848 (s) THF 1964 (ms), 1872 (m), 1851 (s) decalin
	Se	dark red	523	1956 (m), 1845 (s) THF 1961 (ms), 1872 (m), 1850 (s) decalin
	Te	red	488	1950 (m), ~1860 (sh), 1844 (s) THF 1957 (ms), 1875 (m), 1851 (s) decalin
Ta	O	green	595[b]	1951 (m), 1825 (s) THF
	S	dark red	514	1954 (m), 1837 (s) THF 1958 (ms), 1846 (m), 1841 (s) decalin

[a] In toluene, unless otherwise noted. [b] In THF.

Kinetics of tht Substitution of $CpM(CO)_3tht$ (tht = C_4H_8S). The reactions of $CpM(CO)_3tht$ (M = V, Nb, Ta) in toluene proceeded according to eq 4 to give the monosubstituted products $CpM(CO)_3PR_3$. The reactions

$$CpM(CO)_3tht + PR_3 \rightarrow CpM(CO)_3PR_3 + tht \qquad (4)$$

$$M = V, Nb, Ta; PR_3 = P(n\text{-}Bu)_3, PMe_2Ph, P(OPh)_3$$

were monitored by IR spectroscopy (M = V) or by UV-visible spectroscopy (M = V, Nb, Ta). Analysis of the UV-visible kinetic solutions at $t = \infty$ by IR spectroscopy showed that only the monosubstituted products were present (as identified by comparison to the known compounds).[17] This indicated that no photochemical reaction to disubstituted compounds was occurring in the sample chamber. The lack of significant photochemical reaction was also supported by the observation that the rates for M = V were found to be the same for the IR- and UV-

Table IV. Rates of Reaction of $CpV(CO)_3tht$ (Eq 4) with Phosphines in Toluene

temp, °C	L	[L], M	10^3k_{obsd} s^{-1}
31.0	$P(n\text{-}Bu)_3$	0.214	7.21
		0.336	6.86
	$P(OPh)_3$	0.336	6.71
24.7	$P(OPh)_3$	0.336	3.91
		0.336	4.01
		0.336	3.67
17.2	$P(n\text{-}Bu)_3$	0.161	1.54
		1.605	1.33
		0.134	1.60[a]
		0.669	1.53[a]
		1.338	1.52[a]
	$P(OPh)_3$	0.140	1.48
		0.336	1.39
		0.763	1.49
10.1	$P(OPh)_3$	0.336	0.724
		0.336	0.744
		0.336	0.734

[a] Determined by UV–visible at λ = 523 nm.

Table V. First- and Second-Order Rate Constants for the Reaction (Eq 4) of $CpM(CO)_3(C_4H_8E)$ with Phosphines[a]

M	E	temp, °C	L	k_1, s^{-1}	k_2, s^{-1} M^{-1}
V	S	10.1		7.34×10^{-4}	
		17.2		1.45×10^{-3}	
		24.7		3.86×10^{-3}	
		31.0		6.93×10^{-3}	
Nb	O[b]	11.0	$P(n\text{-}Bu)_3$	c	3.9×10^{-1}[d]
			PPh_3	c	5.2×10^{-2}[d]
			$P(OPh)_3$	c	1.9×10^{-2}[d]
Nb	S	49.1	$P(n\text{-}Bu)_3$	1.23×10^{-4}	4.30×10^{-4}
			PMe_2Ph		2.35×10^{-3}
		60.0	$P(OPh_3)$	3.70×10^{-4}	1.73×10^{-4}
			$P(n\text{-}Bu)_3$	3.83×10^{-4}	1.07×10^{-3}
			PMe_2Ph		5.67×10^{-3}
		70.5	$P(n\text{-}Bu)_3$	1.40×10^{-3}	2.07×10^{-3}
			PMe_2Ph	1.63×10^{-3}	1.24×10^{-2}
Nb	Se	70.5	$P(n\text{-}Bu)_3$	4.1×10^{-4}	1.37×10^{-3}
		81.9	$P(OPh)_3$	1.59×10^{-3}	5.2×10^{-4}
			$P(n\text{-}Bu)_3$	1.50×10^{-3}	2.83×10^{-3}
		92.0	$P(n\text{-}Bu)_3$	4.05×10^{-3}	6.23×10^{-3}
Nb	Te[e]	100.8	$P(n\text{-}Bu)_3$	1.74×10^{-4}	4.87×10^{-4}
		110.5	P(n-Bu)3	5.18×10^{-4}	1.02×10^{-3}
		117.5	$P(OPh)_3$	1.06×10^{-3}	$<2 \times 10^{-4}$
			$P(n\text{-}Bu)_3$	1.10×10^{-3}	1.69×10^{-3}
Ta	O	10.2	$P(OPh)_3$	2.1×10^{-4}	1.39×10^{-3}
		20.0	$P(OPh)_3$	8.1×10^{-4}	2.93×10^{-3}
			$P(n\text{-}Bu)_3$		3.06×10^{-2}
		30.3	$P(OPh)_3$	2.65×10^{-3}	7.2×10^{-3}
Ta	S	80.9	PMe_2Ph	1.34×10^{-4}	6.91×10^{-4}
		92.0	$P(OPh)_3$	5.35×10^{-4}	$<2 \times 10^{-5}$
			$P(n\text{-}Bu)_3$	5.31×10^{-4}	1.78×10^{-4}
			PMe_2Ph	5.58×10^{-4}	1.41×10^{-3}
		100.8	PMe_2Ph	1.46×10^{-3}	2.43×10^{-3}

[a] In toluene, unless otherwise noted. [b] In THF. [c] Could not be determined. [d] From plots of k_{obsd} versus $[PR_3]$, where [THF] = 11.1 M. [e] In decalin.

visible-monitored experiments (Table IV). It appeared at first that $CpNb(CO)_3PBu_3$ was the exception to this because significant amounts of $CpNb(CO)_2(PBu_3)_2$ were observed in the IR spectra of the final solution. However, it was soon determined that the disubstituted product was formed when the sample cells were exposed to room light for 30–60 min before the IR spectra were collected. Samples protected from excess room light showed virtually no $CpNb(CO)_2(PBu_3)_2$.

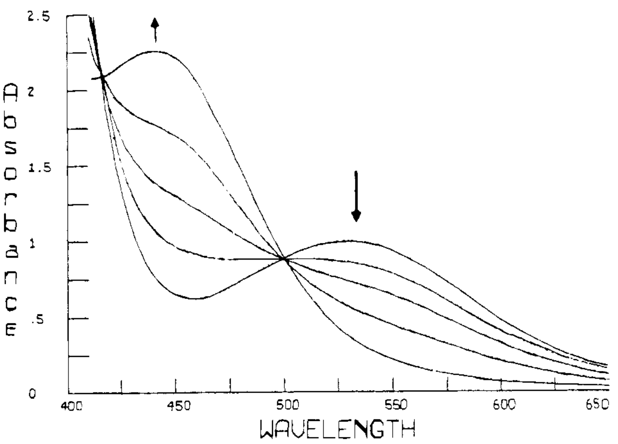


Figure 3. Visible spectral changes for the reaction between $CpNb(CO)_3tht$ and $P(n\text{-}Bu)_3$ in toluene at 60 °C.

Values of k_{obsd} were obtained from the visible spectra by monitoring the decrease of a wavelength at or near the maximum absorption of the starting metal carbonyl. A representative example of the spectral changes in the visible region during the kinetic runs is given in Figure 3. The results for $CpV(CO)_3tht$, as determined by both IR and UV–visible spectroscopy, showed that this complex, like $CpV(CO)_4$, undergoes ligand substitution by a first-order rate law dependent only on the concentration of the substrate. Thus, the k_{obsd} values summarized in Table IV show no dependence upon the concentration of the entering nucleophile. The results for $CpM(CO)_3tht$ where M = Nb or Ta are also analogous to the results observed for $CpM(CO)_4$ (M = Nb, Ta). For these complexes, plots of k_{obsd} versus ligand concentration follow a two-term rate law (eq 3) where one term (k_1) is zero order in entering ligand while the other term (k_2) is first order in entering ligand. A summary of the first- (k_1) and second-order (k_2) rate constants obtained from the plots is given in Table V. A summary of the activation parameters is given in Table VI. These results show that the only major difference between the reaction of $CpM(CO)_4$ and of $CpM(CO)_3tht$ is that the tht-containing compounds react at about 100 °C lower temperatures.

Kinetics of C_4H_8E Substitution of $CpNb(CO)_3(C_4H_8E)$ (E = O, Se, Te) and $CpTa(CO)_3(C_4H_8O)$. The reactions of $CpNb(CO)_3(C_4H_8E)$ where E = Se or Te and of $CpTa(CO)_3(C_4H_8O)$ were analogous to those for E = S (previous section). The replacement of the C_4H_8E ligand by phosphines again occurred by a two-term rate law (eq 3). The first- (k_1) and second-order (k_2) rate constants derived from the plots of k_{obsd} versus concentration of ligand are given in Table V. Activation parameters are given in Table VI.

The situation was different when M = Nb and E = O. The compound $CpNb(CO)_3THF$ was found to rapidly

Table VI. Kinetic Parameters for Substitution Reactions of $CpM(CO)_3(C_4H_8E)$ (Eq 4) with Phosphines

M	E	$\Delta H_1^{\ddagger}$, kcal/mol	$\Delta S_1^{\ddagger}$, esu	L	$\Delta H_2^{\ddagger}$, kcal/mol	$\Delta S_2^{\ddagger}$, esu
V	S	18.3 ± 0.8	-8.2 ± 1.9			
Nb	S	24.3 ± 0.9	-1.2 ± 2.7	$P(n\text{-}Bu)_3$	15.5 ± 0.7	-25.8 ± 1.8
				PMe_2Ph	16.5 ± 0.9	-19.6 ± 2.8
Nb	Se	26.0 ± 0.9	1.4 ± 2.5	$P(n\text{-}Bu)_3$	16.9 ± 1.0	-22.9 ± 2.9
Nb	Te	31.6 ± 2.4	8.2 ± 6.4	$P(n\text{-}Bu)_3$	20.9 ± 1.6	-18.2 ± 4.1
Ta	O	21.0 ± 1.5	-1.3 ± 5.0	$P(OPh)_3$	13.4 ± 0.5	-24.3 ± 1.6
Ta	S	30.8 ± 1.7	10.4 ± 2.4	PMe_2Ph	15.8 ± 0.9	-28.6 ± 1.7

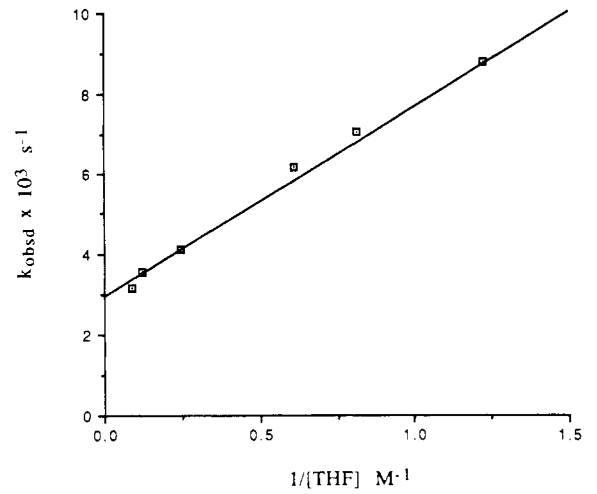
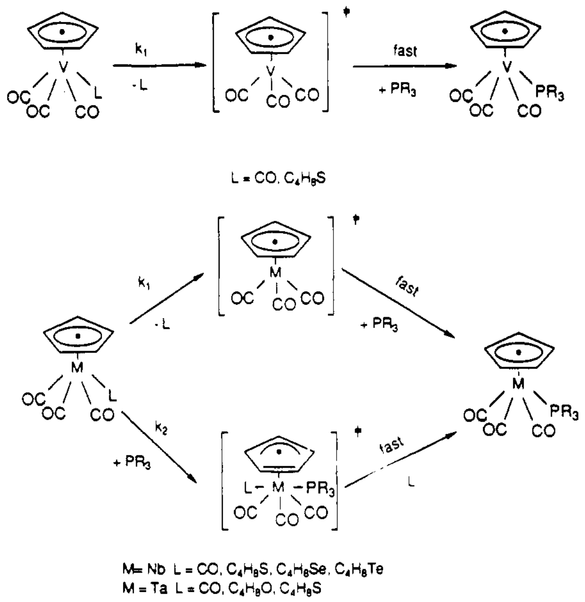


Figure 4. Plot of k_{obsd} versus 1/[THF] for the reaction of $CpNb(CO)_3THF$ with 0.127 M $P(OPh)_3$ in THF/CH_2Cl_2 at 11.0 °C.

Scheme I



decompose in solvents other than THF, making it necessary to run the kinetic reactions in THF. The plots of k_{obsd} versus $[PR_3]$ in 11.1 M THF showed only first-order behavior on the concentration of phosphine, with the intercepts of the lines being zero within experimental error. However, by varying the concentration of THF while holding the concentration of phosphine constant, a plot of k_{obsd} versus 1/[THF] (Figure 4) showed a linear increase in k_{obsd} as the concentration of THF decreased.

Discussion

Triad Studies. The kinetics for CO substitution of $CpM(CO)_4$ and for tht substitution of $CpM(CO)_3tht$ (M = V, Nb, Ta) were found to parallel each other (Scheme I). When M = V, both compounds were observed to react by a dissociative (k_1) mechanism, but when M = Nb and Ta, parallel dissociative (k_1) and associative (k_2) pathways were observed. This change in behavior upon going from V to Nb and Ta can be attributed to the larger size of the Nb and Ta centers. The presence of the larger metal centers decreases the amount of steric crowding that a "$CpML_5$" transition state/intermediate would experience, making an associative pathway more accessible. The presence of five ligands about a CpTa center has been shown possible by the isolation of $CpTa(CO)_2Cl_2(THF)$ and related compounds.[18] The $CpML_5$ intermediate requires that the Cp ligand undergo an $\eta^5 \rightarrow \eta^3$ slippage in order to maintain an 18-electron count of the metal center. This change in mechanisms within a triad is not restricted to group 5; the series $Cp_2M(CO)_2$ (M = Ti, Zr, Hf) shows similar behavior.[2a] Ligand substitution reactions for M = Ti were observed to proceed by a dissociative mechanism, while for M = Zr and Hf only an associative mechanism was observed. Again, the larger size of the Zr and Hf centers compared to Ti is believed to be responsible for the change in mechanism.[2b] One reviewer makes the interesting point that "a changing facility toward slippage may contribute to the changing tendency toward associative reactions as a triad is desended." Unfortunately, we know of no evidence on this point.

Table VII. Values of k_1 for the Dissociative Reactions of $CpM(CO)_4$ and $CpM(CO)_3tht$ Extrapolated to 20 °C

$CpM(CO)_4$			$CpM(CO)_3tht$		
M	k_1	rel rate	M	k_1	rel rate
V	3.8×10^{-11}	2.9×10^6	V	2.2×10^{-3}	1.7×10^5
Nb	5.7×10^{-14}	4.4×10^3	Nb	2.5×10^{-6}	1.9×10^2
Ta	1.3×10^{-17}	1	Ta	1.3×10^{-8}	1

The most surprising result of this study was the observation that the first-row metal (vanadium) compounds were more reactive than the second-row metal (niobium) compounds. This holds for both the $CpM(CO)_4$ and $CpM(CO)_3tht$ series, giving the reactivity order V > Nb > Ta instead of the order Nb > V > Ta expected from the triad rule. This same trend is also observed in the $\Delta H_1^‡$ values (Tables II and VI), where the vanadium compounds have the lowest $\Delta H_1^‡$ values for ligand dissociation and the tantalum compounds the highest. Extrapolation of the k_1 values for both series of compounds to 20 °C (Table VII) shows that the vanadium compounds react approximately 10^3 times faster than the niobium compounds and 10^5–10^6 times faster than the tantalum compounds. At present, there is no clear reason as to why the vanadium complexes are the most reactive. Comparison of the structures of $CpV(CO)_4$[19] versus $CpNb(CO)_4$[13a] and $CpV(CO)_3(SMe_2)$ versus $CpNb(CO)_3(SMe_2)$[10] reveal no significant differences other than those due to the larger Nb versus V center. Thus, the average M–CO bonds increase by ca. 0.15 Å and the metal–cyclopentadienyl plane distance increases by ca. 0.17 Å for the $CpM(CO)_3(SMe_2)$ complexes, with similar differences in the $CpM(CO)_4$ compounds. These similarities suggest that electronic factors are responsible for the unexpected reactivity.

For both series of compounds, the increase in $\Delta H_1^‡$ is fairly uniform, averaging ca. 6 kcal/mol for $CpM(CO)_3tht$ and ca. 5 kcal/mol for $CpM(CO)_4$ upon going from V to Nb and Nb to Ta.[20] The $\Delta S_1^‡$ values are all positive for $CpM(CO)_4$, as expected for a dissociative reaction. However, the $\Delta S_1^‡$ values for $CpM(CO)_3tht$ range from −8 for V to +10 esu for Ta. The negative values of $\Delta S_1^‡$ for V and Nb are somewhat surprising considering the reaction appears to be dissociative. It could be that the equilibrium

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[18] Kwon, D.; Curtis, M. D. *Organometallics* **1990**, *9*, 1.

[19] Wilford, J. B.; Whitla, A.; Powell, H. M. *J. Organomet. Chem.* **1967**, *8*, 495.

[20] One of the reviewers took the trouble to plot values of $\Delta H_1^‡$ versus $\Delta S_1^‡$ for some of the systems and made the following comment. "The trends in the activation parameters are a bit more regular even than the authors suggest. The data for V, Nb, and Ta (E = S) complexes, and for the Nb (E = Se and Te) complexes, all lie on a respectable isokinetic plot with an isokinetic temperature of ca. 430 °C. The reaction mechanisms must all show systematic changes along the series and the rates are obviously 'enthalpy controlled'."

between free and bound ligand observed for $CpNb(CO)_3THF$ could be playing some part in the reaction; however, the lack of rate dependence upon the concentration of phosphine for $CpV(CO)_3tht$ would seem to rule out any major contribution from an equilibrium in these reactions.

It is also possible that the low $\Delta S_1^\ddagger$ values are due to the reaction proceeding by an interchange-dissociative (I_d) mechanism rather than a S_N1 mechanism. In the I_d mechanism, the molecule has already begun to interact with the incoming ligand before the leaving ligand has completely been dissociated, although bond breaking makes a much larger contribution to the energetics in the transition state for reaction than does bond making between the metal and the entering ligand. Such interaction could serve to lower the $\Delta S_1^\ddagger$ value of the reaction. Participation of a solvento complex could also play a part. Studies have shown[21,22] that coordinatively unsaturated organometallic compounds can rapidly coordinate solvents, even so-called noncoordinating solvents such as hydrocarbons. The solvent is then replaced by the incoming ligand to yield the final product. The reason for the low $\Delta S_1^\ddagger$ values is unclear at present. However, these results do demonstrate the problems that can arise when trying to pinpoint a reaction mechanism using $\Delta S^\ddagger$ values.

The values of $\Delta H_2^\ddagger$ and $\Delta S_2^\ddagger$ are all in the expected ranges, with smaller $\Delta H_2^\ddagger$ values and negative values for $\Delta S_2^\ddagger$. One interesting feature of the $\Delta H_2^\ddagger$ values is that they are approximately the same for Nb and Ta when the leaving group is the same.

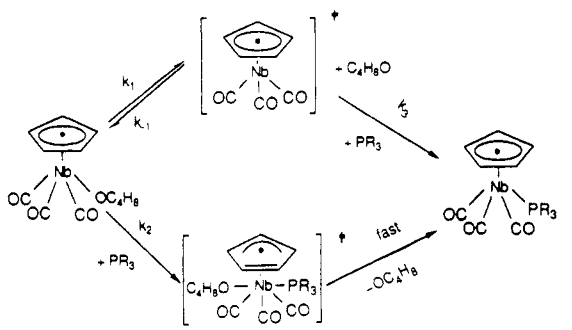
One other interesting feature about these complexes is the relative ratios between the associative and dissociative reactions. Examination of the rates for both Nb and Ta complexes given in Tables I and V indicates that the associative pathway is aided by the presence of the dialkyl chalcogenide ligand compared to the carbonyl. For example, at 150 °C for $CpNb(CO)_4$ with PBu_3, the ratio $k_1{:}k_2$ is 1.3:0.73, while for $CpNb(CO)_3tht$ with PBu_3 at 49.1 °C the ratio $k_1{:}k_2$ is 1.2:4.3. The origin of this enhancement of the associative reaction by the dialkyl chalcogenide ligand is unclear, but it may be involved with stabilization of the $[\eta^3\text{-}CpML_5]^\ddagger$ intermediate by the additional electron density supplied by the chalcogenide ligand compared to the CO ligand.

Chalcogenide Studies. The chalcogenide complexes $CpNb(CO)_3(C_4H_8E)$ (E = S, Se, Te) and $CpTa(CO)_3THF$ were also found to react by the mechanism given in Scheme I, where both dissociative (k_1) and associative (k_2) pathways were observed. When M = Nb and E = O, however, the mechanism changes. In almost neat THF solution (see Experimental Section), the reaction of $CpNb(CO)_3THF$ follows a second-order rate law (eq 5). This suggests an associative pathway as the rate-determining step (eq 6). However, when the PR_3 concentration is kept constant and the THF concentration is changed, the rate of reaction increases with decreasing concentration of THF. In fact, a plot of k_{obsd} versus 1/[THF] is linear (Figure 4) and gives a non-zero intercept at infinite concentration of THF. Such a plot is consistent with a dissociative steady-state preequilibrium (eq 7), followed by addition of the entering PR_3 to afford the product (eq 8).

$$-d[CpNb(CO)_3THF]/dt = k_2[CpNb(CO)_3THF][PR_3] \quad (5)$$

$$CpNb(CO)_3THF \xrightarrow[+PR_3]{k_2} CpNb(CO)_3(PR_3)THF \xrightarrow[\text{fast}]{-CO} CpNb(CO)_3PR_3 \quad (6)$$

Scheme II



$$CpNb(CO)_3THF \underset{-k_1}{\overset{k_1}{\rightleftharpoons}} \text{“}CpNb(CO)_3\text{”} + THF \quad (7)$$

$$\text{“}CpNb(CO)_3\text{”} + PR_3 \xrightarrow{k_3} CpNb(CO)_3PR_3 \quad (8)$$

The steady-state k_{obsd} is then given by eq 9. A combination of eqs 5 and 9 gives k_{obsd} for the overall reaction (eq 10). The reaction pathways consistent with this rate law are represented in Scheme II. This reaction scheme is supported by the linear plot (Figure 4) of k_{obsd} versus 1/[THF] at a constant concentration (0.127 M $P(OPh)_3$) of entering ligand to form the product $CpNb(CO)_3(P(OPh)_3)$. The non-zero intercept of 2.9×10^{-3} s^{-1} is the value of $k_2[P(OPh)_3]$, which then means that $k_2 = 2.3 \times 10^{-2}$ s^{-1}. This is in good agreement with the value of 1.9×10^{-2} s^{-1} obtained from a plot of k_{obsd} versus $[P(OPh_3)]$ in almost neat (11.1 M) THF solution.

$$k_{obsd} = \frac{k_1 k_3}{k^{-1}[THF]}[PR_3] \quad (9)$$

$$k_{obsd} = \left[\frac{k_1 k_3}{k_{-1}[THF]} + k_2\right][PR_3] \quad (10)$$

This mechanism in Scheme II for the leaving group C_4H_8E (E = O) closely resembles the mechanism for E = S, Se, and Te analogues in Scheme I. The only difference is the appearance of the k_{-1} and k_3 terms due to the steady-state formation of "$CpNb(CO)_3$". Thus, all four members of the $CpNb(CO)_3(C_4H_8E)$ series react by a similar mechanism, showing both dissociative and associative pathways.

The results of this study also demonstrate that the stability for the complexes increases in the order O < S < Se < Te. The increase in stability upon going to the heavier chalcogenides is believed to be due to a greater σ-donating ability of the heavier chalcogenide. Evidence for this increasing σ-donor ability comes from the IR spectra of these complexes. The frequency of the CO bands of the complexes decreases in the order S > Se > Te, implying an increase in electron density at the metal center supplied by the chalcogenide ligand (Table III). This trend has also been observed in the compounds $CpV(CO)_3(EMe_2)$[10] and $M_2(CO)_6(\mu\text{-}E_2Ph_2)$[23] (M = Mn, Re).

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Thus, as the frequency of the CO bands decreases, the Nb–E bond strength increases.

It would appear that oxygen is the exception to the above statement. The complex $CpNb(CO)_3(C_4H_8O)$ is clearly the most reactive (and hence the least stable) of the series, but it has the lowest CO frequencies. This is also observed for the corresponding V and Ta compounds. The CO frequencies of $CpTa(CO)_3(C_4H_8O)$ (1951, 1825 cm^{-1}) and of unstable $CpV(CO)_3(C_4H_8O)$ (1952, 1850 cm^{-1})[11] are lower than the CO frequencies of the corresponding S analogues (Ta 1954, 1837; V 1957, 1856 cm^{-1}). This discrepancy can be explained by examining the nature of the $M-ER_2$ bond. For the ether THF, the bond is formed by the donation of one of the two sets of lone electron pairs to the metal center. This donation of a lone pair of electrons also forms the basis of the bond for the thio-, seleno-, and telluroethers as well. However, these elements also have empty d orbitals that are capable of accepting electron density from the metal center. This introduces a small amount of π character into the bond, which both helps to strengthen the bond and to raise the CO frequencies, thus giving the observed order of ν_{CO} as S > Se > Te > O. However, the small differences in the CO frequencies indicates that the π-accepting ability is not very large, which is consistent with the known poor σ- and π-bonding properties of the group 16 ligands.[12]

The stability sequence of O < S < Se < Te for the $CpNb(CO)_3(C_4H_8E)$ series is demonstrated by the observed values of $\Delta H_1^{\ddagger}$, which increase from E = S to E = Te, with Se appearing to behave more like S than Te. A $\Delta H_1^{\ddagger}$ value for E = O could not be obtained, but the high reactivity of $CpNb(CO)_3THF$ indicates that $\Delta H_1^{\ddagger}$ for E = O is qualitatively much smaller than $\Delta H_1^{\ddagger}$ for E = S. The direct comparison of the O and S ligands was possible for the Ta complexes, which are more stable than the Nb complexes. The compound $CpTa(CO)_3THF$, unlike the Nb analogue, could be isolated from THF by removal of the solvent in vacuo and dissolved in toluene. However, while the complex is not stable in toluene (decomposes; $t_{1/2}$ ca. 4.2 min at 25 °C), it was possible to study the kinetics of THF exchange with phosphines. The $\Delta H_1^{\ddagger}$ value obtained for E = O is ca. 10 kcal/mol less than when E = S, a larger difference than the ca. 7 kcal/mol difference observed for changing S to Te in the Nb series. A similar trend is also observed in the $\Delta H_2^{\ddagger}$ values, which increase as the labile O and S ligands are replaced by the more strongly bound chalcogenide ligands. As expected, the differences in the $\Delta H_2^{\ddagger}$ values upon changing the chalcogenide ligand are smaller than the corresponding $\Delta H_1^{\ddagger}$ values, reflecting the contribution of the phosphine in the associative reaction to the overall energetics of the reaction. Lastly, the stability sequence O < S < Se < Te has been observed in other compounds as well. Equilibria studies show the same order for the complexes $TaCl_5(EMe_2)$[24] and $AuBr(EMe_2)$.[25] In addition, the order S < Se < Te was observed for $CpV(CO)_3(EMe_2)$,[10] $M_2(CO)_6(\mu\text{-}Br)_2(\mu\text{-}E_2Ph_2)$ (M = Mn, Re),[23] and Ag^+ complexes of $E(CH_2CH_2CO_2H)_2$.[26]

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Appendix[27]

Referring to the extensive amount of work[21] done by several groups on the very rapid (picosecond) solvation reactions that take place in solution after coordinatively unsaturated "$Cr(CO)_5$" is produced, the reviewer states "While it may be too much to expect Basolo to completely rewrite the discussion, I do believe that organometallic kineticists would be very interested to know what he thinks of these developments. At least some substantial footnote indicating his overall reactions would be helpful."

In spite of these elegant experiments,[21] including studies[22] of Cr–alkane bond strengths by time-resolved photoacoustic calorimetry, I think it is still useful to distinguish between "dissociative" and "associative" ligand substitution of metal complexes in solution. There will always be borderline cases, but the gross distinction remains clear. The term "dissociation" is used when the energetics of ligand replacement largely involves M–L bond breaking, where L is the leaving group. Certainly at some stage of M–L bond stretching there is some involvement of the solvent (or entering nucleophile) to complete the M–L bond cleavage. However, if the energy contribution of the entering solvent (or ligand) is small, then it is useful to refer to the reaction pathway as dissociative. The experimental rate law would show zero-order dependence on the entering nucleophile. The term "associative" is used when the rate law shows a first-order dependence on the entering nucleophile and when nuclephilic strengths can vary as much as 10^6 times or more.

Dissociation is not intended to mean in a literal sense a "coordinatively unsaturated" or a "naked metal" intermediate. Surely, as a ligand leaves, going into solution, it does not create a vacuum at the spot vacated; solvent moves in to occupy the "open" spot. Pearson and I[28] stated this in the first edition of our book in 1958 where we discuss the conversion of $[Co(NH_3)_6]^{3+}$ into $[Co(NH_3)_5(H_2O)]^{3+}$.

The present experiments being done by various research groups,[21,22] including the effect of pressure[2b] on rates of reaction, are an attempt to understand the intimate details of the mechanisms of ligand substitution in metal complexes. My generation of researchers on this topic looked at the gross aspects of the mechanisms, and the terminology introduced of "dissociative" and "associative" remains valid and useful today. Keep in mind that physical organic chemistry had a long history on solvolysis/substitution reactions, all the way from S_N1 and S_N2 to considering ion pairs, solvent separated ion pairs, etc.

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