concentration of $AlMe_3$ at $t = 0$ was calculated from the relative integrals of the C_5H_5 and Ti–Me signals of $Cp_2TiMeCl{\cdot}Al$ and the total integral of the AlMe signal. Least squares analysis of second-order plots of ln kt vs. t yielded the rate constants. This procedure was repeated for several concentrations of the titanium and aluminum reagents and at several different temperatures. Activation parameters were obtained from least squares analysis of ln k/T vs. $1/T$ plots.

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Registry No. 1, 67719-69-1; 2, 79269-70-8; 3, 33071-07-7; 4, 87738-99-6; 5, 87729-04-2; 6, 38496-87-6; 7, 1282-43-5; 8, 87729-05-3; 9, 87739-00-2; 10, 87739-01-3; 11, 87729-06-4; 12, 87729-07-5; $CpTiCl_3$, 1270-98-0; $TiCl_4$, 7550-45-0; Cp_2TiCl_2, 1271-19-8; $[C_5H_4(CH_3)]_2TiCl_2$, 1282-40-2; $Cp^{tms}Li$, 76514-39-1; ⟨Cp⟩Li, 87729-03-1; CpLi, 16733-97-4; Cp^*TiCl_3, 12129-06-5; $Cp_2Ti(O\text{-}t\text{-}Bu)_2$, 87729-08-6; $Cp_2TiMeCl$, 1278-83-7; Cp_2TiMe_2, 1271-66-5; Cp_2TiF_2, 309-89-7; methylcyclopentadienyllithium, 54061-45-9; (1,3-diphenylcyclopentadienyl)lithium, 58813-26-6; ^1H-indenyllithium, 32334-19-3; trimethylaluminum, 75-24-1.

Highly Reduced Organometallics. 16.[1] Synthesis, Isolation, and Characterization of the Tricarbonylcyclopentadienylmetalate(2−) Anions of Niobium and Tantalum, $C_5H_5M(CO)_3{}^{2-}$

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Treatment of $C_5H_5M(CO)_4$ (M = Nb, Ta) with sodium in liquid ammonia at −78 °C generates the corresponding disodium salts $Na_2[C_5H_5M(CO)_3]$, which have been spectroscopically identified. Cesium iodide reacts with $Na_2[C_5H_5M(CO)_3]$ in liquid ammonia to provide 70–80% isolated yields of pale orange, air-sensitive solids that analyze satisfactorily as the unsolvated dicesium salts $Cs_2[C_5H_5M(CO)_3]$. These are the first isolated salts containing the tricarbonylcyclopentadienylmetalate dianions of niobium and tantalum. Reactions of $C_5H_5M(CO)_3{}^{2-}$ with CH_3CN, Et_4N^+, or other weak Brønsted acids or Ph_3SnCl provide, after cation exchange, 40–70% isolated yields of $[Et_4N][C_5H_5M(CO)_3H]$ or $[Et_4N][C_5H_5M(CO)_3SnPh_3]$, which are characterized by elemental analyses and IR and ^1H NMR spectra.

Introduction

For over 20 years, the only example of a cyclopentadienyl-substituted metal carbonyl dianion was $C_5H_5V(CO)_3{}^{2-}$,[2] originally prepared by Fischer and Vigoureux,[3] by the method shown in eq 1. Very recently,

$$C_5H_5V(CO)_4 + 2Na \xrightarrow{NH_3} Na_2[C_5H_5V(CO)_3] + CO \qquad (1)$$

$Na_2[C_5H_5Nb(CO)_3]$ has also been identified by IR spectroscopy as a product formed during the reduction of $C_5H_5Nb(CO)_4$ by Na–Hg in THF.[5] In this paper, we report the characterization and first isolation of salts containing $C_5H_5M(CO)_3{}^{2-}$ (M = Nb, Ta) as well as triphenylstannyl and hydride derivatives of these highly reactive materials. These dianions are likely to be important precursors to a variety of new organoniobium and organotantalum complexes, including mixed-metal clusters containing these elements.

Experimental Section

General Procedures and Materials. All operations were performed under an atmosphere of nitrogen further purified by passage through columns of activated BASF catalyst, anhydrous magnesium perchlorate, and molecular sieves. Solutions were transferred via stainless steel cannulas and syringes; otherwise reactions were generally performed by using standard Schlenk apparatus with a double manifold vacuum line. Ammonia was dried with Na metal and distilled in vacuo directly into the reaction vessel. Reagent grade acetonitrile was dried with CaH_2, freed of oxygen by a nitrogen purge, and distilled immediately before use. Reagent grade tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were distilled from alkali-metal benzophenone ketyls before use. Reagent grade acetone, heptane, absolute ethanol, and isopentane were freed of oxygen by purging with nitrogen for 1–2 h before use. Published procedures for the synthesis of $C_5H_5M(CO)_4$ (M = Nb, Ta),[6] $[Na(diglyme)_2][M(CO)_6]$,[7] and $[Na(DME)]C_5H_5$[8] were employed. All other reactants and solvents were obtained from commercial sources and used without further purification.

Dicesium Tricarbonylcyclopentadienyltantalate(2−), $Cs_2[C_5H_5Ta(CO)_3]$ (1). Liquid ammonia (100 mL) was distilled into a flask containing a glass stir bar, $C_5H_5Ta(CO)_4$ (0.50 g, 1.40 mmol), and sodium metal (0.10 g, 4.2 mmol) at −70 °C. Within 1.5 h after the reaction mixture had warmed to −33 °C, the initial blue solution had changed to an orange color. This solution of $Na_2[C_5H_5Ta(CO)_3]$ was filtered at −70 °C into a flask containing a glass stir bar and a solution of CsI (1.45 g, 5.58 mmol) in 10 mL of liquid ammonia. After about 2–3 min a finely divided orange solid precipitated. The orange slurry was filtered at −70 °C, washed with liquid ammonia (1 × 75 mL, 1 × 50 mL), and dried

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Table I. IR Spectrum of Products in the Carbonyl Stretching Frequency Region

compound	medium	ν(CO), cm^{-1}
$Cs_2[C_5H_5Ta(CO)_3]$	Nujol	1736 s, 1570 s, br
$Na_2[C_5H_5Ta(CO)_3]^a$	HMPA	1740 s, 1620 s, 1590 sh
$Cs_2[C_5H_5Nb(CO)_3]$	Nujol	1738 s, 1576 s, br
$Na_2[C_5H_5Nb(CO)_3]^a$	HMPA	1740 s, 1601 s, br
$[Et_4N][C_5H_5Ta(CO)_3H]$	Nujol	1892 s, 1780 sh, 1760 s, br
	CH_3CN	1900 s, 1780 s, br
$[Et_4N][C_5H_5Nb(CO)_3H]$	Nujol	1895 s, 1785 s, 1770 s, br
	CH_3CN	1898 s, 1790 s, br
$[Et_4N][C_5H_5Ta(CO)_3SnPh_3]$	Nujol	1890 s, 1795 m-s, 1765 s, br
	CH_3CN	1895 s, 1780 s, br
$[Et_4N][C_5H_5Nb(CO)_3SnPh_3]$	Nujol	1890 s, 1790 m-s, 1765 s, br
	CH_3CN	1898 s, 1785 s, br

[a] Not isolated as analytically pure substances.

under vacuum. In this manner 0.63 g (76%) of a pale orange, air-sensitive solid was obtained that analyzed satisfactorily for compound 1 without further treatment. The compound decomposes without melting above 250 °C.

Anal. Calcd for $C_8H_5Cs_2O_3Ta$: C, 16.11; H, 0.85; Cs, 44.61. Found: C, 16.10; H, 0.77; Ta, 44.90.

Dicesium Tricarbonylcyclopentadienylniobate(2−), $Cs_2[C_5H_5Nb(CO)_3]$ (2). An essentially identical procedure was used to prepare a sample of $Cs_2[C_5H_5Nb(CO)_3]$ of satisfactory purity. From 0.60 g (2.56 mmol) of $C_5H_5Nb(CO)_4$, 2.66 g (10.2 mmol) of CsI, and 0.177 g (7.68 mmol) of sodium metal was obtained 0.78 g (68%) of pale orange and flaky, air-sensitive compound 2. It decomposes without melting above 250 °C.

Compound 2, like 1, is insoluble in practically all unreactive solvents and only slightly soluble in hexamethylphosphoramide (HMPA).

Anal. Calcd for $C_8H_5Cs_2NbO_3$: C, 18.92; H, 0.99. Found: C, 18.68; H, 1.06.

Tetraethylammonium Tricarbonylcyclopentadienylhydridotantalate(1−), $[Et_4N][C_5H_5Ta(CO)_3H]$ (3). Exactly the same procedure and quantities of reactants as described above were used to prepare an ammonia solution of $Na_2[C_5H_5Ta(CO)_3]$. After filtration and evaporation of the ammonia, a 0.35-g sample of yellow-orange powdery and air-sensitive solid was obtained. Elemental analysis for this material were not obtained but its infrared spectrum (Table I) is entirely consistent with that expected for $Na_2[C_5H_5Ta(CO)_3]$. To a 0.33-g quantity of this solid was added 40 mL of anhydrous acetonitrile. After the mixture was stirred for 1 h, $[Et_4N]Br$ (0.20 g, 0.96 mmol) was added. After being stirred for an additional 6 h, the solution was filtered (medium porosity fritted disk) to provide a clear yellow solution. After removal of solvent in vacuo, the resulting residue was washed with water (3 × 20 mL). The product was then dried in vacuo to yield 0.25 g (43% based on $C_5H_5Ta(CO)_4$) of yellow-orange and crystalline 3. This material melts at 183 °C with decomposition and gave satisfactory analyses for compound 3 without further purification.

Anal. Calcd for $C_{16}H_{26}NO_3Ta$: C, 41.66; H, 5.68; N, 3.04. Found: C, 41.54; H, 5,71; N, 3.01.

In subsequent syntheses of 3, higher yields (60–80%) have been obtained by omitting the isolation of $Na_2[C_5H_5Ta(CO)_3]$ and protonating the disodium salt generated in situ.

Tetraethylammonium Tricarbonylcyclopentadienylhydridoniobate(1−), $[Et_4N][C_5H_5Nb(CO)_3H]$ (4). Cold anhydrous acetonitrile (40 mL at −40 °C) was added to a cold liquid ammonia solution (−40 °C) of $Na_2[C_5H_5Nb(CO)_3]$, prepared in situ from 0.32 g (1.4 mmol) of $C_5H_5Nb(CO)_4$ and 0.090 g (4.1 mmol) of sodium metal at −78 °C in 60 mL of liquid ammonia. Tetraethylammonium bromide (0.32 g, 1.5 mmol) was added via a bent Schlenk tube, and the solution was warmed to room temperature. After filtration, the solution was bright yellow and all solvent was removed. The resulting solid was washed thoroughly with H_2O (3 × 10 mL) and dried to provide 0.30 g (68% based on $C_5H_5Nb(CO)_4$) of crystalline yellow 4 of satisfactory purity.

Anal. Calcd. for $C_{16}H_{26}NNbO_3$: C, 51.48; H, 7.02; N, 3.75. Found: C, 51.31; H, 6.82; N, 3.74.

Compound 4 melts with decomposition at 175–177 °C. After we had finished this work, Rehder and co-workers reported the synthesis of the same substance, but undoubtedly in impure form (cf. Discussion), by a somewhat different procedure.[5]

Tetraethylammonium Tricarbonylcyclopentadienyltriphenylstannyltantalate(1−), $[Et_4N][C_5H_5Ta(CO)_3SnPh_3]$ (5). A cold solution of Ph_3SnCl (0.96 g, 2.5 mmol) in 40 mL of THF was added dropwise at −40 °C into a cold (−40 °C) liquid ammonia solution of $Na_2[C_5H_5Ta(CO)_3]$, prepared in situ from the sodium metal reduction of $C_5H_5Ta(CO)_4$ (0.89 g, 12.5 mmol) as described previously. Solid $[Et_4N]Br$ (0.58 g, 2.7 mmol) was added all at once with a bent Schlenk tube into the reaction mixture. The solution was then slowly warmed to room temperature while the ammonia evaporated. Filtration of this solution through a medium porosity fritted disk produced a clear golden yellow solution. After all but 10 mL of the solvent was removed under reduced pressure, 30 mL of ethyl ether was added, thereby producing a golden yellow precipitate. This was washed with additional ether (2 × 30 mL) and crystallized from acetone–ether to provide 1.10 g (58%) of microcrystalline compound 5 of satisfactory purity. Compound 5 is only slightly air sensitive and decomposes without melting above 130 °C.

Anal. Calcd for $C_{34}H_{40}NO_3SnTa$: C, 47.26; H, 5.29; N, 1.84. Found: C, 47.63; H, 4.86; N, 1.97.

Tetraethylammonium Tricarbonylcyclopentadienyltriphenylstannylniobate(1−), $[Et_4N][C_5H_5Nb(CO)_3SnPh_3]$ (6). The same procedure for the synthesis of compound 5 was employed in the preparation of 6. From the sodium metal reduction of $C_5H_5Nb(CO)_4$ (0.50 g, 2.13 mmol) in liquid ammonia, $Na_2[C_5H_5Nb(CO)_3]$ was obtained. To this solution was added Ph_3SnCl (0.82 g, 2.13 mmol) in THF and then $[Et_4N]Br$ (0.49 g, 2.3 mmol). From this reaction mixture was obtained 0.69 g (55% yield) of golden yellow and slightly air-sensitive compound 6 of satisfactory purity (decomposition above 130 °C).

Anal. Calcd for $C_{34}H_{40}NNbO_3Sn$: C, 53.44; H, 5.98; N, 2.08. Found: C, 53.65; H, 5.59; N, 1.90.

Results and Discussion

In recent years, our research group has systematically investigated the reduction of substituted mononuclear metal carbonyls.[1,9] On the basis of previous observations concerning the reductions of $C_5H_5V(CO)_4$,[3,10] $C_5H_5Mn(CO)_3$,[10] and $C_5H_5Re(CO)_3$,[4] it was clearly of interest to extend this study to the cyclopentadienyl-substituted carbonyls of niobium and tantalum. Also, our recently developed atmospheric pressure synthesis of $Nb(CO)_6^-$ and $Ta(CO)_6^-$,[7] facilitated this study since these are excellent precursors to the neutral derivatives $C_5H_5M(CO)_4$.[6]

Synthesis, Isolation, and Characterization of $C_5H_5Nb(CO)_3^{2-}$ and $C_5H_5Ta(CO)_3^{2-}$. Sodium metal reductions of $C_5H_5Nb(CO)_4$ and $C_5H_5Ta(CO)_4$ in liquid ammonia at −33 °C proceed rapidly to provide the corresponding disodium salts $Na_2[C_5H_5M(CO)_3]$ (eq 2). No attempts were made to obtain elemental analyses on these yellow-orange pyrophoric substances so it is not known whether they are solvated, but their infrared spectra in hexamethylphosphoramide (HMPA) (see Table I) are so

$$C_5H_5M(CO)_4 + 3Na \xrightarrow[-33\ ^\circ C]{NH_3} Na_2[C_5H_5M(CO)_3] + {}^1/_2\ Na_2C_2O_2 \quad (2)$$

$$M = Nb, Ta$$

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(9) (a) Chen, Y.-S.; Ellis, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 1141. (b) Chen, Y.-S.; Ellis, J. E. *Ibid.* **1983**, *105*, 1689. (c) Lin, J. T.; Hagen, G. P.; Ellis, J. E. *Ibid.* **1983**, *105*, 2296. (d) Rochfort, G. A.; Ellis, J. E. *J. Organomet. Chem.* **1983**, *250*, 265.

(10) Ellis, J. E.; Faltynek, R. A.; Hentges, S. G. *J. Organomet. Chem.* **1976**, *120*, 389.

similar to that reported for $Na_2[C_5H_5V(CO)_3]$[10] that there is no doubt concerning the identitiy of the anions in these salts. Our spectra also compare favorably to that reported previously for $Na_2[C_5H_5Nb(CO)_3]$ in THF.[10] The latter was obtained as an impure solid (contaminated by $Na[C_5H_5Nb(CO)_3H]$) from the reduction of $C_5H_5Nb(CO)_4$ by Na/Hg in THF and was reported after our work in this area was completed. We find that the reduction of $C_5H_5M(CO)_4$ (M = Nb, Ta) by Na–NH_3 is far superior to the Na/Hg–THF method in that only traces of the hydride are obtained, provided the synthesis is conducted under rigorous anaerobic conditions.

Treatment of the filtered liquid ammonia solutions of $Na_2[C_5H_5M(CO)_3]$ with 2 equiv of cesium iodide provided 60–80% yields of very thermally stable (decomp pt >250 °C) pale orange solids that gave satisfactory elemental analysis for unsolvated $Cs_2[C_5H_5M(CO)_3]$ (M = Nb, Ta) (eq 3). These materials are analogous to $Cs_2[C_5H_5V(CO)_3]$,

$$Na_2[C_5H_5M(CO)_3] + 2CsI \xrightarrow{NH_3} Cs_2[C_5H_5M(CO)_3]\downarrow + 2NaI \quad (3)$$

$$M = Nb, Ta$$

reported by Fischer et al. many years ago,[3] and represent the first well-characterized salts containing the cyclopentadienyltricarbonylmetalate dianions of niobium and tantalum. It is worth noting that these three dianions are presently the only definitely established examples of compounds of the general formula $C_5H_5M(CO)_x^{2-}$. Whether it is possible to prepare bona fide examples of dianions of this type for which $x = 2$ (M = Mn, Tc, Re) is presently unknown.[11]

Synthesis and Spectroscopic Properties of $C_5H_5Nb(CO)_3H^-$ and $C_5H_5Ta(CO)_3H^-$. Treatment of $C_5H_5M(CO)_3^{2-}$, prepared in situ from the reduction of $C_5H_5M(CO)_4$ with Na–NH_3, with 1 equiv of water or alcohols or anhydrous acetonitrile provides 60–80% isolated yields of the monohydrides $C_5H_5Nb(CO)_3H^-$ and $C_5H_5Ta(CO)_3H^-$ (eq 4). These were isolated as Et_4N^+ salts that gave

$$C_5H_5M(CO)_3^{2-} + H^+ \xrightarrow{NH_3} C_5H_5M(CO)_3H^- \quad (4)$$

$$M = Nb, Ta$$

satisfactory analyses for the unsolvated compounds. Earlier Rehder and co-workers reported analogous reactions of $C_5H_5V(CO)_3^{2-}$[12] and $C_5H_5Nb(CO)_3^{2-}$[5] with CH_3CN which provided $C_5H_5V(CO)_3H^-$ and $C_5H_5Nb(CO)_3H^-$.[13] The latter anion was isolated by Rehder et al. as the tetraethylammonium salt. Although the infrared spectrum for their material is in satisfactory agreement with ours (Table I), the poor carbon analysis (Calcd: C, 51.5. Found: C, 45.2.) Dull color (ochre) of the solid, incorrect color of its solution in acetonitrile (green), and incompatible ^1H NMR spectrum (two resonances in the C_5H_5 region) indicate their material is substantially impure. By comparison, bona fide substantially pure and markedly air-sensitive $[Et_4N][C_5H_5Nb(CO)_3H]$ is a bright yellow crystalline substance that dissolves in acetonitrile to provide a yellow solution and has only a singlet in the C_5H_5 region of its ^1H NMR spectrum (Table II). This latter feature is entirely consistent with similar spectra observed for $C_5H_5V(CO)_3H^-$[14] and $C_5H_5Ta(CO)_3H^-$ (Table II). The ^1H NMR spectrum of $[Et_4N][C_5H_5Nb(CO)_3H]$ contains a very broad hydride resonance (Table II) that is shown in Figure 1. A similarly broad signal in the ^{93}Nb NMR spectrum of $C_5H_5Nb(CO)_3H^-$ was reported in Rehder's study.[5]

Table II. ^1H NMR Spectra of Anionic Derivatives of $C_5H_5M(CO)_3^{2-}$ (M = Nb, Ta)

compound	medium	δ
$[Et_4N][C_5H_5Ta(CO)_3H]$[a]	CD_3CN	−6.1 (s, TaH), 5.4 (s, C_5H_5)
$[Et_4N][C_5H_5Nb(CO)_3H]$[b]	CD_3CN	−5.9 (br, NbH), 5.3 (s, C_5H_5)
$[Et_4N][C_5H_5Ta(CO)_3SnPh_3]$[c]	CD_3CN	5.4 (s, C_5H_5), 7.2–7.6 (m, C_6H_5)
$[Et_4N][C_5H_5Nb(CO)_3SnPh_3]$[c]	CD_3CN	5.4 (s, C_5H_5), 7.2–7.6 (m, C_6H_5)

[a] The hydride resonance is sharp. Resonance positions for $(C_2H_5)_4N^+$ occur at δ 1.2 (t of t, NCH_2*CH_3*) and 3.1–3.3 (q, N*CH_2*). [b] A 300-MHz spectrometer was used to locate the broad hydride resonance (see Figure 1). Resonance positions for $(C_2H_5)_4N^+$ are at δ 1.1 (t of t, NCH_2*CH_3*) and 3.1–3.4 (q, NCH_2). Our ^1H NMR spectrum of $C_5H_5Nb(CO)_3H^-$ is not in agreement with that previously reported for this substance (cf. Discussion).[5] [c] Resonance positions of the cation are virtually identical with those observed for the hydrides (cf. footnotes *a* and *b*).

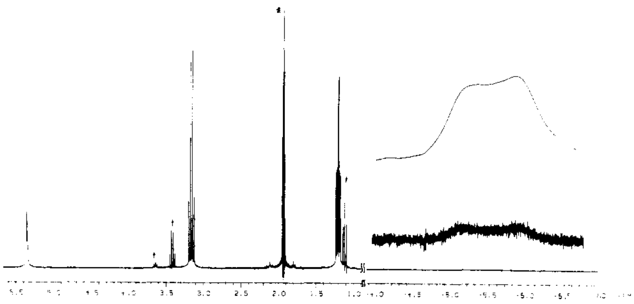

Figure 1. ^1H NMR spectrum of $[Et_4N][C_5H_5Nb(CO)_3H]$ in CD_3CN. See Table II for resonance positions. Asterisked signal is due to CD_2HCN. Signals due to impurities are indicated by daggers (†).

Infrared and ^1H NMR data for the previously unknown $[Et_4N][C_5H_5Ta(CO)_3H]$ (Tables I and II) are very similar to that of the niobium analogue except the metal hydride resonance is a sharp singlet and is easily observed.

Synthesis and Properties of $C_5H_5Nb(CO)_3SnPh_3^-$ and $C_5H_5Ta(CO)_3SnPh_3$. To provide further confirmation of our synthesis of $C_5H_5Nb(CO)_3^{2-}$ and $C_5H_5Ta(CO)_3^{2-}$, the disodium salts, generated in situ, were treated with 1 equiv of Ph_3SnCl (eq 5). After cation exchange and re-

$$C_5H_5M(CO)_3^{2-} + Ph_3SnCl \rightarrow C_5H_5M(CO)_3SnPh_3^- \quad (5)$$

$$M = Nb, Ta$$

crystallization, 50–60% isolated yields of golden yellow compounds, which gave satisfactory analyses for $[Et_4N][C_5H_5M(CO)_3SnPh_3]$ (M = Nb, Ta), were obtained. These materials have infrared spectra (Table I) and ^1H NMR spectra (Table II) which are entirely consistent with these formulations. A previously reported infrared spectrum of $[Et_4N][C_5H_5V(CO)_3SnPh_3]$ (ν(CO) 1891 s, 1795 s(br) cm^{-1})[10] in HMPA is very similar to those of the niobium and tantalum analogues except the latter have

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(11) While the isolation of $[Et_4N]_2[C_5H_5Re(CO)_2]$ has been recently reported, we have been informed (Bergman, R. G., private communication, 1983) that the infrared spectrum reported for this substance is that of $C_5H_5Re(CO)_2H^-$ (Yang, G. K., Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 6500).

(12) Puttfarcken, U.; Rehder, D. *J. Organomet. Chem.* **1980**, *185*, 219.

(13) We also find that anhydrous $[Et_4N]Br$ reacts completely within 12 h with $Na_2[C_5H_5M(CO)_3]$ (M = Nb and Ta) in THF at room temperature to generate the hydride anions $C_5H_5M(CO)_3H^-$.

(14) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, 100, 7902.

corresponding ν(CO) values at somewhat higher energies.

Concluding Remarks. The sodium in liquid ammonia reduction of cyclopentadienyltetracarbonylniobium and -tantalum provides the corresponding $Na_2[C_5H_5M(CO)_3]$ that may be isolated as the very thermally stable dicesium salts $Cs_2[C_5H_5M(CO)_3]$. This is the first isolated compound of satisfactory purity containing the niobium dianion and the first report on the substituted tantalum dianion. These materials have been further characterized by their conversion to monoanionic hydrides and triphenylstannyl derivatives, which have been isolated as pure tetraethylammonium salts for the first time. Further studies on the chemical properties of these highly reactive substances are in progress.

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Registry No. 1, 87801-25-0; 2, 87801-26-1; 3, 87801-28-3; 4, 84950-24-3; 5, 87801-30-7; 6, 87801-32-9; $Na_2[C_5H_5Ta(CO)_3]$, 87801-33-0; $Na_2[C_5H_5Nb(CO)_3]$, 84950-22-1; $C_5H_5Ta(CO)_4$, 32628-95-8; $C_5H_5Nb(CO)_4$, 12108-03-1; CsI, 7789-17-5; $[Et_4N]Br$, 71-91-0; Ph_3SnCl, 639-58-7.

X-ray Crystal and Molecular Structures of the Monomeric 1:1 Adducts of Diphenyltin(IV) Dichloride and Trimethyltin(IV) Chloride with 2,6-Dimethylpyridine (2,6-Lutidine) *N*-Oxide

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Diphenyltin(IV) dichloride–2,6-dimethylpyridine *N*-oxide (I), $C_{19}H_{19}Cl_2NOSn$, forms colorless crystals, mp 159 °C, in the triclinic space group $P\bar{1}$ with a = 9.359 (2) Å, b = 10.534 (2) Å, c = 10.996 (3) Å, α = 97.46 (2)°, β = 114.74 (2)°, γ = 93.26 (2)°, V = 968.8 (3) Å^3, Z = 2, and ρ = 1.60 g cm^{-3}. The structure was determined from 3609 reflections collected on a Nicolet R3 diffractometer with monochromatic Mo Kα radiation and refined to a final R value of 0.0253 for the 3102 reflections included in the least-squares sums. The monomeric complex contains five-coordinated, trigonal-bipyramidal tin with the phenyl rings forming an angle of 124.1 (1)° in the equatorial plane. The ligand oxygen and one of the chlorine atoms occupy the apical positions at an angle of 172.8 (1)°. The sum of the angles subtended at the tin atom in the trigonal plane is 359.0 (3)°. The tin atom is displaced from this plane by 0.1279 (2) Å in the direction of the chlorine atom. The $Sn-Cl_{eq}$ bond [2.366 (1) Å] is shorter than the $Sn-Cl_{ax}$ bond [2.471 (1) Å]. The Sn–O distance is 2.296 (2) Å, and the two Sn–C bond distances are approximately equal [2.119 (3) and 2.128 (4) Å]. Trimethyltin(IV) chloride–2,6-dimethylpyridine *N*-oxide (II), $C_{10}H_{18}ClNOSn$, mp 106 °C, also crystallizes as colorless crystals in the same space group with a = 8.174 (2) Å, b = 9.599 (2) Å, c = 9.895 (3) Å, α = 115.33 (2)°, β = 105.50 (2)°, γ = 81.45 (2)°, V = 675.7 (2) Å^3, Z = 2, and ρ = 1.58 g cm^{-3}. This structure was solved from 2437 reflections and refined to a final R value of 0.0283 for the 2207 reflections that were used in the least-squares sums. The molecule has the tin atom in a trigonal-bipyramidal geometry with the methyl carbons in the trigonal plane. The Sn–C bond distances are 2.119 (5), 2.120 (4), and 2.125 (6) Å, and the C–Sn–C angles are 114.1 (2), 121.8 (3), and 123.1 (2)°, giving a sum of 358.9 (3)°. The apical Cl–Sn–O angle is 177.4 (1)°, and the tin atom is displaced from the trigonal plane by 0.2357 (2) Å toward the chlorine atom. Both the Sn–Cl and Sn–O distances are larger than those found in structure I [2.533 (1) and 2.400 (2) Å, respectively)]. The angle at the oxygen atom is 125.7 (2)° in I and 130.6 (2)° in II, and the angle formed by the Sn–O–N system and the pyridine *N*-oxide ring is 86.98 (4)° in I and 84.75 (16)° in II. The N–O distances are 1.346 (4) Å in I and 1.326 (4) Å in II.

We have discovered that the 1:1 adducts formed by diorganotin(IV) dihalides with certain pointed ligands containing the >C═O, >C═S, >S═O, ⩾N→O, or ⩾P═O grouping are in fact six coordinated.[1] The structures of the 1:1 dimethyltin(IV) dichloride complexes with diphenylcyclopropenone[2] and with 2,6-dimethylpyridine (2,6-lutidine) *N*-oxide[3] reveal dimer formation through bridging chlorine atoms, and the structure of the 1:1 salicylaldehyde adduct[4,5] can be reinterpreted in similar terms as an associated solid with bridging phenolic oxygen atoms. Only a single example of a true five-coordinated 1:1 adduct has been reported: diphenyltin(IV) dichloride–benzthiazole.[6]

Di-[7] and trimethyltin(IV)[8] chlorides are themselves associated in the solid state through bridging chlorine atoms,

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