Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE CHEMISTRY OF THE GROUP V METAL CARBONYLS IV*. MIXED METAL SEVEN-COORDINATE COMPLEXES

A. DAVISON AND J. E. ELLIS**

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

(Received August 12th, 1971)

SUMMARY

The preparation of the main group mixed metal complexes $(C_6H_5)_3SnM(CO)_6$, $(C_6H_5)_3SnM(CO)_5(C_6H_5)_3P$, $(C_6H_5)_3SnM(CO)_4[(C_6H_5)_2PCH_2]_2$; $(C_6H_5)_3PAuM(CO)_6$, $(C_6H_5)_3PAuM(CO)_5(C_6H_5)_3P$; $C_2H_5HgM(CO)_6$, $C_2H_5HgM(CO)_5(C_6H_5)_3P$ where M = V, Nb or Ta is described. The unsubstituted complexes are very prone to heterolytic cleavage in weak donor solvents. This behavior, as well as that for the phosphine substituted complexes, is discussed in relationship to the synthesis of mixed metal complexes.

INTRODUCTION

In a previous communication[1] we have briefly reported the preparation of some seven-coordinate derivatives of vanadium, niobium, and tantalum. Initially we experienced considerable difficulties in synthesizing certain of these mixed metal species because of their oxidative and thermal instabilities. In addition, main group metal to vanadium bonds in these complexes are markedly susceptible to heterolytic cleavage by weak donor solvents such as THF. We now describe the syntheses and characterization of these species and their reaction chemistry.

Prior to our work there had been two reports of complexes of this type, namely $(C_6H_5)_3PAuV(CO)_6$[2] and $RHgTa(CO)_6$ ($R = CH_3$, C_2H_5 and C_6H_5)[3].

EXPERIMENTAL

General procedures and starting materials

All operations were carried out under a nitrogen atmosphere with the precautions previously described[4]. The purification of ethanol, acetone, water, tetrahydrofuran (THF), benzene, diethyl ether, pentane and heptane was also described therein. Methylene chloride was dried over and distilled from P_2O_5 and then freed of oxygen by purging it with a dispersed stream of nitrogen. Butane was trap-to-trap distilled on a vacuum line before use. With exceptions noted below, all reagents were

---

* For Part III see ref. 4.

** NSF Traineeship 1970–1971

obtained from commercial sources and used without further purification. Ethylmercuric chloride (K and K Laboratories) was sublimed before use. Tetrakis(triphenylphosphine)gold perchlorate[5], and 1,1,1-tris[(diphenylphosphino)methyl]ethane[6], were prepared using published procedures.

(Triphenylphosphine)gold chloride was prepared by the following procedure: a solution of 2.05 g (0.52 mmole) of chloroauric acid ($HAuCl_4 \cdot 3H_2O$) in 70 ml of ethanol was mixed with another containing 2.62 g (1.00 mmole) of triphenylphosphine in 50 ml of ethanol. On gentle heating of the stirred solution fine white crystals formed within minutes. These were filtered, washed with 95% ethanol (2 × 15 ml) and dried (2.02 g, 93% yield, m.p. 239–240° with decomp., lit[5]. 242°).

Bis(diglyme)sodium* hexacarbonylvanadate(–I) and the tris(diglyme)potassium hexacarbonylmetallates(–I) of niobium and tantalum were prepared according to published procedures[7]. The preparation of the various substituted metal carbonyl anions of vanadium, niobium and tantalum were given in the previous paper[4] in this series. The silica gel used in filtrations was of column chromatography grade, 70-375 mesh (E. Merck).

Infrared spectra were recorded on a Perkin–Elmer Model 237 B spectrometer. Melting points were determined on a Kofler hot stage microscope in sealed evacuated capillaries and are uncorrected. Elemental analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Michigan and Mrs. N. F. Alvord of the M.I.T. Microanalytical Laboratory. Molecular weight determinations by osmometry were performed by Midwest Microlab, Inc., Indianapolis, Indiana.

Solvent evaporations and drying operations were done *in vacuo*, at or below room temperature. Prolonged exposure of some of the compounds, particularly the mercury derivatives, to vacuum was avoided.

All reactions were routinely monitored in the metal carbonyl stretching frequency region by infrared spectroscopy. When the bands corresponding to the carbonyl containing reactant disappeared or decreased to a constant intensity the reactions were stopped. The heterolytic cleavage studies described in the discussion section were also monitored by infrared spectroscopy. A direct correspondence between infrared spectral changes and conductivity measurement results has been reported on studies of heterolytic cleavages of other compounds containing a metal–metal bond[8]; accordingly, we have used infrared spectroscopy alone to monitor these cleavages. The production of the substituted and unsubstituted metal carbonyl anions was readily detected by their characteristic, strong absorptions in the carbonyl stretching frequency region. The positions and relative intensities of these absorptions in methylene chloride are virtually the same as those reported previously in THF[4].

(Triphenylstannyl)hexacarbonyltantalum, $(C_6H_5)_3SnTa(CO)_6$

Ice cold methylene chloride (40 ml) was added to a precooled (0°) flask containing 1.63 g (2.06 mmol.) of $[K(diglyme)_3][Ta(CO)_6]$ and 0.794 g (2.06 mmole) of $(C_6H_5)_3SnCl$. The reaction appeared to occur almost immediately after addition of solvent. The contents were stirred for 15 min and then filtered at 0°. After all but 10 ml of solvent had been evaporated, 5 ml of pentane was added. Cooling the resulting air sensitive solution to ca. −70° caused the formation of a dark solid which was

---

* Diglyme = Bis(2-methoxyethyl) ether.

rejected. Subsequent evaporation of solvent from the supernatant liquid caused red crystals to form on the sides of the flask. After all but about 1 ml of solvent had been evaporated the supernatant liquid was removed. The resulting crystalline, orange-red solid was dried at 0°. A yield of 0.50 g (34%) of product (m.p. 80–82° with decomp.) was obtained. (Found: C, 40.94; H, 2.24; Ta, 26.23. $C_{24}H_{15}O_6SnTa$ calcd.: C, 41.25; H, 2.16; Ta, 25.89%.)

(Triphenylstannyl)hexacarbonylniobium, $(C_6H_5)_3SnNb(CO)_6$

Small red plates of the desired product could be isolated at low temperatures (−50°) from the interaction of equivalent amounts of $[K(diglyme)_3][Nb(CO)_6]$ and $(C_6H_5)_3SnCl$ in cold (−20°) methylene chloride; however, these rapidly decomposed to brown tar at room temperature and could be stored for only a few hours at −10° under nitrogen. Because of the thermal instability of this complex, no elemental analyses were obtained for it. However, it was identified by the similarity of its infrared spectrum in CH_2Cl_2 to that of the tantalum complex described above.

(Triphenylstannyl)hexacarbonylvanadium, $(C_6H_5)_3SnV(CO)_6$

A mixture of 1.90 g (3.72 mmole) of $[Na(diglyme)_2][V(CO)_6]$ and 1.43 g (3.72 mmole) of $(C_6H_5)_3SnCl$ was dissolved in 40 ml of methylene chloride at room temperature. No reaction occurred. However, shaking this solution with 30 ml of water caused it to turn orange quickly. After vigorously stirring for 30 min at room temperature the methylene chloride layer was cooled to −50° and filtered through a small column (ca. 30 mm long, 25 mm diameter) of silica gel to give a clear orange red solution. Heptane (5 ml) was added and the solvent was slowly evaporated at room temperature. When all but about 3 ml of solvent had been removed much yellow solid had formed on the sides of the flask. The supernatant liquid was then treated with 15 ml pentane and cooled to −70°. Additional fine yellow solid precipitated. After removing the supernatant liquid, the solid was washed with 15 ml of pentane at −70° and dried at 0°. It was then dissolved at room temperature in 40 ml of methylene chloride/heptane (3/1, v/v). This solution was filtered through a short bed (ca. 10 mm) of silica gel. The resulting filtrate was slowly concentrated. Initially a brown solid came out of solution. This was rejected and separated from the supernatant liquid via a cannula. Slow evaporation of the solvent was continued and resulted in the formation of a bright yellow crystalline substance. The final steps of this procedure are identical with those of the initial crystallization. A yield of 0.52 g (25%) of analytically pure, pale orange-yellow crystals was obtained (m.p. 81–82° with decomp.). (Found: C, 50.74; H, 2.89. $C_{24}H_{15}O_6SnV$ calcd.: C, 50.65; H, 2.66%.)

Solubility and stability properties of $(C_6H_5)_3SnM(CO)_6$, $M = V, Nb, Ta$

As a solid or in solutions the vanadium compound is thermally and oxidatively more stable than the corresponding niobium and tantalum species. Whereas the crystalline tantalum complex quickly chars in air, the vanadium substance can be handled in air briefly. The solid tantalum species decomposes slowly at 0° under an atmosphere of nitrogen, while the vanadium compound can be kept under these conditions indefinitely without deterioration. The vanadium and tantalum compounds are soluble at room temperature in saturated and unsaturated hydrocarbons, methylene chloride and diethyl ether (with partial cleavage). In THF, diglyme, acetone and organic solvents of higher dielectric constant, these compounds undergo complete and reversible heterolytic cleavage. Accordingly, they cannot be conveniently prepared in these solvents.

(Triphenylstannyl)(triphenylphosphine)pentacarbonylvanadium, $(C_6H_5)_3SnV(CO)_5(C_6H_5)_3P$

(*a*). A mixture of 1.45 g (2.84 mmol) of $[Na(diglyme)_2][V(CO)_6]$, 0.915 g (2.84 mmole) of $(C_6H_5)_3SnCl$ and 0.745 g (2.84 mmole) of $(C_6H_5)_3P$ was dissolved in 40 ml of methylene chloride. On addition of 30 ml of water to the above system the methylene chloride layer changed from a greenish-yellow color characteristic of $[V(CO)_6]^{-1}$ to an orange color due to $(C_6H_5)_3SnV(CO)_6$. After the solution had been stirred for ca. 48 h, bands in the infrared region due to $(C_6H_5)_3SnV(CO)_6$ had disappeared. The deep yellow brown methylene chloride layer was then separated from the aqueous layer, cooled to $-60°$ to freeze out dissolved water, and filtered at $-60°$ through a 3 mm column of silica gel. The resulting clear bright red-orange solution was evaporated to dryness leaving a microcrystalline orange solid. Recrystallization of this material from 15 ml of methylene chloride-heptane (4/1, v/v) by slow evaporation of solvent gave 0.32 g (14%) of transparent orange crystals (m.p. 165–170° with decomp.). (Found: C, 61.36; H, 3.64; mol. wt. in benzene, 795. $C_{41}H_{30}O_5PSnV$ calcd.: C, 61.35; H, 3.77%; mol. wt., 803.)

(*b*). It was also possible to obtain $(C_6H_5)_3SnV(CO)_5$ $(C_6H_5)_3P$ in somewhat better yield (35%) by using the same conditions as in (*a*) except the addition of water was omitted. The reaction was allowed to proceed for seven days at room temperature. The solution was subsequently swirled with water (4 x 50 ml) to remove unreacted $[Na(diglyme)_2][V(CO)_6]$ and then worked up as described in (*a*). The solid was finally washed with pentane (4 x 15 ml) to remove unreacted $(C_6H_5)_3SnV(CO)_6$ which formed when water was added in the above step.

(*c*). No reaction occurred when 0.60 g (1.03 mmole) of $[(C_2H_5)_4N][V(CO)_5(C_6H_5)_3P]$ and 0.40 g (1.03 mmole) of $(C_6H_5)_3SnCl$ were dissolved in 20 ml of methylene chloride. However, stirring the solution with 20 ml of water at room temperature promoted a reaction, after 4 h virtually all $[V(CO)_5(C_6H_5)_3P]^{-1}$ had disappeared. The brown-orange methylene chloride layer was worked up as in (*a*) to yield 0.31 g (38%) of orange crystals. These gave solution and mull infrared spectra and a melting point which were identical to those of genuine $(C_6H_5)_3SnV(CO)_5(C_6H_5)_3P$.

(Triphenylstannyl)(triphenylphosphine)pentacarbonyltantalum, $(C_6H_5)_3SnTa(CO)_5(C_6H_5)_3P$

Cold (0°) methylene chloride (40 ml) was added to a mixture of 1.15 g (1.46 mmole) $[K(diglyme)_3][Ta(CO)_6]$, 0.562 g (1.46 mmole) $(C_6H_5)_3SnCl$ and 0.382 g (1.46 mmole) of $(C_6H_5)_3P$. The reaction mixture was stirred for $\frac{1}{2}$ h at 0° and filtered. Concentration of the orange-red solution caused red crystals to form on the sides of the flask. After only ca. 2 ml of solution remained, the supernatant liquid was removed from the solid. This was washed with pentane (2 x 10 ml) and dried at room temperature. A yield of 0.95 g(70%) of deep red crystals was obtained. The compound was purified by passing a solution of 0.70 g of the above solid in 35 ml methylene chloride/heptane (6/1, v/v) through a 5 mm column of silica gel. Slow evaporation of this solution afforded 0.45 g of deep red crystals. These were washed with pentane (3 x 10 ml) and dried (dec. ca. 180–185°). (Found: C, 52.70; H, 3.16; mol. wt. in benzene, 913. $C_{41}H_{30}O_5PSnTa$ calcd.: C, 52.80; H, 3.24%; mol. wt., 933.)

The same compound was also prepared by interaction of equivalent amounts of $[(C_2H_5)_4N][Ta(CO)_5(C_6H_5)_3P]$ and $(C_6H_5)_3SnCl$ in methylene chloride at −20°. In contrast to the corresponding vanadium reaction, no addition of water was required to promote formation of the product.

(Triphenylstannyl)(triphenylphosphine)pentacarbonylniobium, $(C_6H_5)_3SnNb(CO)_5(C_6H_5)_3P$

Ice-cold methylene chloride (30 ml) was added to a mixture of 1.10 g (1.57 mmole.) of $[K(diglyme)_3][Nb(CO)_6]$, 0.61 g (1.57 mmole) of $(C_6H_5)_3SnCl$ and 0.63 g (1.57 mmole) of $(C_6H_5)_3P$. The color of the solution after seconds had changed from a red to a deep chocolate brown. The work-up and recrystallization of the product were performed exactly the same way as for the tantalum compound. The recrystallized orange-red microcrystalline product amounted to 0.35 g (25%) (m.p. 180–182° with decomp.) (Found: C, 57.85; H, 3.74. $C_{41}H_{30}NbO_5PSn$ calcd.: C, 58.27; H, 3.58%.)

This substance was also prepared by reacting equivalent amounts of $[(C_6H_5)_4As][Nb(CO)_5(C_6H_5)_3P]$ and $(C_6H_5)_3SnCl$ in methylene chloride at −20° in the absence of water. Although solutions of the tantalum and niobium complexes are quite air sensitive, the crystalline solids, unlike $(C_6H_5)_3SnTa(CO)_6$, can be handled briefly in air without any deleterious effect. They are, however, more prone to oxidation than the analogous vanadium compound. While all the compounds are only very slightly soluble in saturated hydrocarbons they are soluble without dissociation in benzene, methylene chloride, THF, acetone, and ethyl acetate.

(Triphenylstannyl)tetracarbonyl[1,2-bis(diphenylphosphino)ethane]tantalum, $(C_6H_5)_3SnTa(CO)_4[(C_6H_5)_2PCH_2]_2$

(*a*). The addition of 50 ml of methylene chloride to a mixture of 0.670 g (0.85 mmole) of $[K(diglyme)_3][Ta(CO)_6]$ 0.326 g (0.85 mmole) of $(C_6H_5)_3SnCl$ and 0.338 g (0.85 mmole) of 1,2-bis(diphenylphosphino)ethane gave an initially cherry red solution due to the formation of $(C_6H_5)_3SnTa(CO)_6$. Within 5 min at room temperature the color of the stirred solution had faded to a light orange-yellow. Ten minutes later, heptane (5 ml) was added, the solution was filtered and then evaporated to dryness. The resulting orange-yellow solid was washed with pentane (2 × 10 ml) and dried. The solid was recrystallized from methylene chloride/heptane to give 0.768 g (87%) of analytically pure, crystalline, orange-yellow solid (darkens above 210°). (Found: C, 55.34; H, 3.75; P. 5.41. $C_{48}H_{39}O_4P_2SnTa$ calcd.: C, 55.35; H, 3.78; P, 5.95%.)

(*b*). Methylene chloride (20 ml) at room temperature was added to a mixture of 0.410 g (0.50 mmole) of $[(C_2H_5)_4N]\{Ta(CO)_4[(C_6H_5)_2PCH_2]_2\}$ and 0.192 g (0.50 mmole) of $(C_6H_5)_3SnCl$. The solution immediately turned to a pale orange color. After addition of 5 ml of heptane the solution was evaporated completely. The solid was taken up in benzene (90 ml), filtered to remove insoluble $(C_2H_5)_4NCl$ and then evaporated to dryness. The resulting solid was recrystallized from the minimum amount of methylene chloride/heptane (6/1, v/v) and worked up, as in part (*a*), to give 0.416 g (80%) of orange-yellow crystals which gave identical infrared spectra to those from the solid obtained by route (*a*).

(Triphenylstannyl)tetracarbonyl[1,2-bis(diphenylphosphino)ethane]vanadium, $(C_6H_5)_3SnV(CO)_4[(C_6H_5)_2PCH_2]_2$

(*a*). A mixture of 1.01 g (1.98 mmol) of $[Na(diglyme)_2][V(CO)_6]$, 0.76 g (1.98 mmole) of $(C_6H_5)_3SnCl$ and 0.787 g (1.98 mmole) of 1,2-bis(diphenylphosphino)ethane was stirred in 40 ml of benzene. No detectable reaction occurred within seven days at room temperature. Subsequently, the benzene solution was shaken repeatedly with water until the aqueous phase became nearly colorless. While the benzene solution remained over 50 ml of water for another week, crystals of product began to form on the sides of the flask. The organic phase was then separated and evaporated to dryness. The resulting solid was recrystallized from the minimum amount of methylene chloride/heptane (4/1, v/v) to give 0.816 g (45%) of yellow crystalline product (darkens above 210°). (Found: C, 63.17; H, 4.28; P, 6.65. $C_{48}H_{39}O_4P_2SnV$ calcd.: C, 63.26; H, 4.30; P. 6.80%.)

A mixture of 0.40 g (0.58 mmole) of $[(C_2H_5)_4N]\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}$ and 0.22 g (0.58 mmole) of $(C_6H_5)_3SnCl$ was dissolved in 20 ml of ice cold methylene chloride. The product was then worked up at room temperature by the identical procedure used for the corresponding tantalum reaction. A yield of 0.35 g (66%) of light yellow crystals was obtained.

(Triphenylstannyl)tetracarbonyl[1,2-bis(diphenylphosphino)ethane]niobium, $(C_6H_5)_3SnNb(CO)_4[(C_6H_5)_2PCH_2]_2$

A mixture of 0.40 g (0.57 mmol) of $[K(diglyme)_3][Nb(CO)_6]$, 0.22 g (0.57 mmole) of $(C_6H_5)_3SnCl$ and 0.23 g (0.57 mmole) of 1,2-bis(diphenylphosphino)ethane was dissolved in 25 ml of cold (−20°) methylene chloride/heptane (4/1, v/v). The solution was then allowed to warm slowly with stirring over a period of 2 h to +10°. The solution was then worked up at room temperature by the identical procedure used for the corresponding tantalum reaction. The recrystallized product consisted of 0.44 g (81%) of bright yellow solid (darkens above 170°). (Found: C, 60.17; H, 4.21. $C_{48}H_{39}NbO_4P_2Sn$ calcd.: C, 60,47; H, 4.11%.)

The solubility properties of $(C_6H_5)_3SnM(CO)_4[(C_6H_5)_2PCH_2]_2$ (M=V, Nb and Ta) are quite similar. They are insoluble in saturated hydrocarbons, carbon tetrachloride, diethyl ether, alcohols and water, slightly soluble in acetonitrile and nitromethane and soluble in aromatic hydrocarbons, methylene chloride, carbon disulfide, THF, ketones and esters.

(Triphenylstannyl)(tri-n-butylphosphine)pentacarbonylvanadium, $(C_6H_5)_3SnV(CO)_5(n\text{-}C_4H_9)_3P$

A mixture of 0.879 g (1.72 mmole) of $[Na(diglyme)_2][V(CO)_6]$, 0·664 g (1.72 mmole) of $(C_6H_5)_3SnCl$ and 0.348 g (1.72 mmole) of $(n\text{-}C_4H_9)_3P$ was dissolved with stirring in 30 ml of methylene chloride. After 10 h much sodium chloride had precipitated and the solution had become orange. Subsequently, it was filtered and evaporated to a viscous oil which partially solidified overnight in a refrigerator. The oily substance solidified completely on trituration with pentane (10 ml) at −50°. The solid was purified by dissolving as much of it as possible in pentane (50 ml) and then filtering. The orange filtrate was slowly evaporated; yellow crystalline solid readily formed during this process. When all but ca. 1 ml of solution was evaporated the supernatant liquid was cooled to −50° and separated from the solid. The crystals were then washed with small portions of pentane (3 × 2 ml) at −50° and dried. A yield of 0.638 g (50%) of light orange-red crystals was obtained (m.p. 118-120° with decomp.). (Found: C, 56.91; H, 5.55. $C_{35}H_{42}O_5PSnV$ calcd.: C, 56.55; H, 5.70%.)

This substance is much more air sensitive both as a crystalline solid and in solutions than the other seven-coordinate phosphine derivatives of vanadium described in this paper. The analytical sample turned to a black brown solid after an exposure of 10 min to dry air. Except for its much larger solubility in saturated hydrocarbons its solubility properties resemble those of the (triphenylstannyl)(triphenylphosphine)pentacarbonylmetal complexes.

(Triphenylstannyl)(triphenylphosphite)pentacarbonyltantalum, $(C_6H_5)_3SnTa(CO)_5(C_6H_5O)_3P$

A solution of 0.218 g (0.705 mmole) of $(C_6H_5O)_3P$ in ice cold methylene chloride (20 ml) was added via a cannula to a mixture of 0.557 g (0.705 mmole) of $[K(diglyme)_3][Ta(CO)_6]$ and 0.272 g (0.705 mmole) of $(C_6H_6)_3SnCl$. After 5 h of stirring at room temperature, all of the intermediate $(C_6H_5)_3SnTa(CO)_6$ had disappeared. Heptane (5 ml) was added, the orange-red solution was passed through 10 mm of silica gel and then slowly evaporated. An orange oil was obtained which solidified overnight in a refrigerator. The solid was washed with pentane (2 × 10 ml) and dried. This material was recrystallized from 25 ml of methylene chloride/heptane (4/1, v/v). When all but 3 ml of solvent had been evaporated, the supernatant liquid was cooled to 0° and treated with 10 ml of pentane. The solid was then separated from the supernatant liquid, and washed with 10 ml additional pentane at 0° and dried. An orange microcrystalline product (0.435 g) was thereby obtained in 63% yield (m.p. 138–139° with decomp.). (Found: C, 49.89; H, 3.31; P, 3.05. $C_{41}H_{30}O_8PSnTa$ calcd.: C, 50.18; H, 3.08; P, 3.16%.)

This substance is more air sensitive as a solid or in solutions than the corresponding triphenylphosphine derivative. Its solubility properties closely resemble those of $(C_6H_5)_3SnTa(CO)_6$. The crystalline solid is sufficiently stable to allow it to be stored indefinitely under nitrogen at room temperature.

[(Triphenylphosphine)gold]hexacarbonyltantalum, $(C_6H_5)_3PAuTa(CO)_6$

A slurry of 3.38 g (6.83 mmole) of $(C_6H_5)_3PAuCl$ in 100 ml of THF was added dropwise to a solution of 5.38 g (6.83 mmole) of $[K(diglyme)_3][Ta(CO)_6]$ in 60 ml of THF maintained at 0°. After the addition was complete (45 min) the deep red solution was stirred for an additional 15 min and then filtered. The filtrate was concentrated to 100 ml and pentane (140 ml) was slowly added to the ice cold, stirred solution. On cooling this to −50° orange red crystals formed. These were filtered off at −50°, washed with pentane (2 × 20 ml) and dried. The solid from this crop of crystals (2.28 g) proved to be analytically pure and was not recrystallized. Additional product was obtained from the supernatant liquid by the above procedure giving a total of 4.36 g (80%) of $(C_6H_5)_3PAuTa(CO)_6$ (dec. 120°). (Found: C, 35.76; H, 1.99; mol.wt. in benzene, 830. $C_{24}H_{15}AuO_6PTa$ calcd.: C, 35.56; H, 1.87%; mol.wt., 808.)

[(Triphenylphosphine)gold]hexacarbonylniobium, $(C_6H_5)_3PAuNb(CO)_6$

Methylene chloride (30 ml at −40°) was added to a cold (−40°) mixture of 0.60 g (0.86 mmole) of $[K(diglyme)_3][Nb(CO)_6]$ and 0.42 g (0.86 mmole) of $(C_6H_5)_3$-

PAuCl. The resulting bright red-orange solution was stirred for ½ h while it slowly warmed to 0°. Next 4 ml of heptane was added and the solution was filtered at 0° through a 5 mm column of silica gel. On slow evaporation of the solvent at ca. −5° short red needles of product began to form. When only 2-3 ml of solvent remained, the solution was cooled to −60° and butane (10 ml) was added via a cannula. The solid was separated from the now deep red-brown supernatant liquid, washed with butane (2 x 10 ml) and dried at −20°. A yield of 0.40 g (65%) of dark orange-red crystals was obtained. This solid was purified by careful recrystallization from 25 ml of a methylene chloride/heptane solvent mixture (4/1, v/v). The purity and color of the product were much improved by carrying out all operations below −10°. The resulting solid was washed with butane (3 x 10 ml) at −50° and dried at −25°, giving 0.31 g (50%) of red-orange needles (dec. ca. 125°). (Found; C, 40.13; H, 1.89. $C_{24}H_{15}AuNbO_6P$ calcd.: C, 40.03; H, 2.10%.)

[(Triphenylphosphine)gold]hexacarbonylvanadium, $(C_6H_5)_3PAuV(CO)_6$

A mixture of 0.59 g (1.2 mmole) of $(C_6H_5)_3PAuCl$ and 0.42 g (1.2 mmole) of $[(C_2H_5)_4N][V(CO)_6]$ was dissolved in 40 ml of methylene chloride at room temperature. No reaction occurred. However, when water (60 ml) was added with vigorous shaking the reaction was complete within a minute. The yellow-orange methylene chloride layer was filtered and subsequently evaporated to dryness. The resulting tar was triturated with pentane (15 ml) and dried. Tetraethylammonium chloride was then removed from the product by treating it with benzene (20 ml) and filtering the slurry. The dry solid obtained upon evaporation of the filtrate was then recrystallized from 30 ml of methylene chloride/heptane (5/1, v/v). Slow evaporation of this solution at room temperature readily caused yellow needles of product to form when all but 3 ml of solvent had been removed, the supernatant liquid was separated from the crystalline solid. The latter was washed with pentane (2 x 5 ml) and dried, thereby yielding 0.51 (64%) of analytically pure, orange-yellow product (dec. 134–136°). (Found: C, 42.45; H, 1.94. $C_{24}H_{15}AuO_6PV$ calcd.: C, 42.50; H, 2.23%.)

Essentially quantitative yields of this substance can also be obtained from $[Na(diglyme)_2][V(CO)_6]$ and $(C_6H_5)_3PAuCl$ in THF or methylene chloride in the absence of water.

The compounds $(C_6H_5)_3PAuM(CO)_6$, M = V, Nb and Ta are insoluble in water, slightly soluble in alcohols and saturated hydrocarbons, and soluble in carbon disulfide, aromatic hydrocarbons, methylene chloride, ethers, and acetone. Except for the somewhat greater solubility of the vanadium compound in saturated hydrocarbons, the solubility properties of these substances are virtually identical. In presence of protic solvents the niobium and tantalum compounds slowly decompose.

Tris(triphenylphosphine)gold hexacarbonyltantalate, $\{[(C_6H_5)_3P]_3Au\}[Ta(CO)_6]$

(*a*). A solution of 0.606 g (2.32 mmole) of $(C_6H_5)_3P$ in 10 ml of methylene chloride was added by syringe to 0.374 g (0.46 mmole) of $(C_6H_5)_3PAuTa(CO)_6$ in 15 ml of cold (0°) methylene chloride. After the addition of one equivalent (0.46 mmole) of $(C_6H_5)_3P$ the originally deep red solution paled slightly. An infrared spectrum of the solution showed that a sharp strong band at 1855 cm^{-1} due to $[Ta(CO)_6]^{-1}$ ion had developed.

When a total of five equivalents (2.32 mmole) of $(C_6H_5)_3P$ had been added only traces of $(C_6H_5)_3PAuTa(CO)_6$ remained; the band at 1855 cm^{-1} was now very intense. The color of the solution was orange, which is characteristic of the $[Ta(CO)_6]^{-1}$ ion. No spectral evidence for the formation of $(C_6H_5)_3PAuTa(CO)_5(C_6H_5)_3P$, the originally anticipated product, was observed during the reaction. After 5 ml of heptane had been added, the solution was slowly evaporated to dryness. The resulting yellow-orange solid was washed with heptane (3 x 15 ml) and dried. It was then recrystallized from 25 ml of acetone/ethanol (3/2, v/v) by slowly evaporating the solution under reduced pressure. Crystallization occurred readily; when all but 5 ml of solvent remained the supernatant liquid was separated from the crystals. The highly reflecting, yellow crystalline solid was then washed with ethanol (3 x 5 ml) and dried. A yield of 0.36 g (50%) of analytically pure product was obtained (m.p. 147–150° with decomp.). (Found: C, 54.27; H, 3.37; P, 6.78. $C_{60}H_{45}AuO_6P_3Ta$ calcd.: C, 54.07; H, 3.40; P, 6.97%.)

(*b*). A mixture of 0.400 g (0.30 mmole) of $[(C_6H_5)_3P]_4AuClO_4$ and 0.243 g (0.31 mmole) of $[K(diglyme)_3][Ta(CO)_6]$ was dissolved in 10 ml of acetone. Dropwise addition of water to the magnetically stirred solution caused crystalline product to fall from solution. Water was added until crystal formation ceased. The yellow solid was then washed with water (10 ml) and dried. The product was subsequently recrystallized from acetone/ethanol as in part (*a*) to give 0.285 g (60%) of yellow-orange crystals. The infrared spectra, decomposition point and solubility properties of this substance were identical to those of the analyzed product of part (*a*).

[(Triphenylphosphine)gold](triphenylphosphine)pentacarbonylvanadium, $(C_6H_5)_3PAu\text{-}V(CO)_5(C_6H_5)_3P$

The addition of ice-cold methylene chloride (30 ml) to a mixture of 0.51 g (0.88 mmole) of $[(C_2H_5)_4N][V(CO)_5(C_6H_5)_3P]$ and 0.43 g (0.88 mmole) of $(C_6H_5)_3PAuCl$ gave almost immediately a red solution. After this was stirred for 15 min at 0°, water (15 ml) at 0° was added to extract $[(C_2H_5)_4N]Cl$ from the organic phase. The aqueous layer was subsequently removed, heptane (5 ml) added to the methylene chloride solution and the latter evaporated to dryness. The resulting orange solid was washed with pentane (3 x 15 ml) and dried giving 0.48 g (61%) of product. The analytical sample was prepared by recrystallization of the above solid from 25 ml of methylene chloride/heptane (4/1, v/v), washing the resulting solid with pentane (3 x 15 ml) and finally drying it. Orange crystalline product (dec. ca. 145–150°) was thereby obtained in an overall yield of 40%. (Found: C, 53.94; H, 3.36; mol. wt. in benzene, 840. $C_{41}H_{30}AuO_5P_2V$ calcd.: C, 53.99; H, 3.33%; mol. wt., 912.)

[(Triphenylphosphine)gold](triphenylphosphine)pentacarbonyltantalum, $(C_6H_5)_3PAu\text{-}Ta(CO)_5(C_6H_5)_3P$

Methylene chloride (20 ml at −15°) was added via a cannula to a mixture of 0.25 g (0.35 mmole) of $[(C_2H_5)_4N][Ta(CO)_5(C_6H_5)_3P]$ and 0.174 g. (0.35 mmol) of $(C_6H_5)_3PAuCl$ at −15°. The reaction was complete in seconds. After the solution was stirred for 15 min and allowed to warm to 0°, 15 ml of water (0°) was added. 10 min later the methylene chloride phase was cooled to −50° to freeze out dissolved and suspended water and filtered through a 6 mm column of silica gel at this temperature. The remaining work-up and recrystallization steps are identical to those for the corresponding vanadium compound except for the following. During the latter step the orange-red solution was initially filtered at room temperature through a short (5 mm) silica gel column. It was then evaporated slowly and cautiously to prevent the product from separating as an oil. After all but 2–3 ml of solvent had been removed the solution was cooled to −60°, the supernatant liquid was removed and the crystals were washed with cold (−60°) pentane (3 x 10 ml). The very fine orange-red needles were then dried at 0° (0.13 g, 28%, dec. ca. 160°). (Found: C, 47.40; H, 3.20. $C_{41}H_{30}AuO_5P_2Ta$ calcd.: C, 47.26; H, 2.90%.)

[(Triphenylphosphine)gold](triphenylphosphine)pentacarbonylniobium, $(C_6H_5)_3PAuNb(CO)_5(C_6H_5)_3P$

An essentially complete reaction occurred on adding methylene chloride (20 ml at −60°) to a mixture of 0.26 g (0.29 mmole) of $[(C_6H_5)_4As][Nb(CO)_5(C_6H_5)_3P]$ and 0.145 g (0.29 mmole) of $(C_6H_5)_3PAuCl$. The initial workup was identical to that of the analogous tantalum reaction. However, in the recrystallization step the solutions were kept below −15° to minimize decomposition of the more solvolytically unstable niobium compound. The analytical sample consisted of 0.14 g (48%) of red-orange plates (dec. ca. 150°). (Found: C, 51.64; H, 3.30. $C_{41}H_{30}AuNbO_5P_2$ calcd.: C, 51.60; H, 3.17%.)

The crystalline niobium and tantalum complexes can be handled in air for brief periods without noticeable change; however, their solutions deteriorate quickly in the presence of air. Except for a decreased solubility in saturated hydrocarbons, these compounds have solubility properties similar to those of $(C_6H_5)_3PAuM(CO)_6$ (M=V, Nb, Ta).

(Ethylmercury)hexacarbonylniobium $C_2H_5HgNb(CO)_6$

A cooled (−60°) solution of 25 ml of methylene chloride/heptane (4/1, v/v) was added via a cannula to a mixture of 0.563 g (0.80 mmole) of $[K(diglyme)_3][Nb(CO)_6]$ and 0.212 g (0.80 mmole) of C_2H_5HgCl. The resulting red-orange solution was warmed to −20° within an hour and filtered at this temperature. Some metallic mercury had deposited on the bottom of the reaction vessel; the solution, however, was much less thermally sensitive than that of $(C_6H_5)_3SnNb(CO)_6$. On evaporation of the solvent, red crystals were readily formed. When the solution was concentrated to about 2 ml, it was cooled to −60° and the supernatant liquid was removed. The solid was then washed with pentane (3 x 10 ml) at −60° and dried at −20°. A yield of 0.256 g (65%) of orange-red needles was obtained. The solid can be readily and cleanly sublimed at room temperature (0.05 mm) onto a dry ice/isopropanol cooled probe. The decomposition point (60–63°) of the samples obtained from the first crystallization and the sublimation were identical. (Found: C, 19.87; H, 1.12. $C_8H_5HgNbO_6$ calcd.: C, 19.59; H, 1.03%.)

(Ethylmercury)hexacarbonyltantalum, $C_2H_5HgTa(CO)_6$

This complex was prepared from the reaction of equimolar amounts of $[K(diglyme)_3][Ta(CO)_6]$ and C_2H_5HgCl in methylene chloride by the procedure used for the corresponding niobium complex in 62% yield (m.p. 65–68° with decomp., lit.[3] 65–67°).

(Ethylmercury)hexacarbonylvanadium, $C_2H_5HgV(CO)_6$

A mixture of 0.93 g (1.83 mmole) of $[Na(diglyme)_2][V(CO)_6]$ and 0.486 g

(1.83 mmole) of C_2H_5HgCl was dissolved in 20 ml of cold (–10°) methylene chloride/heptane (3/1, v/v). There was an immediate reaction on addition of solvent. The solution was stirred for $\frac{1}{2}$ h at –10° and then filtered at this temperature. The clear, light-orange filtrate was then evaporated until about 3 ml solvent remained. During this operation fine yellow crystals readily formed. The solution was then cooled to –50°, pentane (5 ml) was added, and the supernatant liquid was separated from the solid. This was washed with 5 ml of pentane at –50° and dried at 0°.

The product was subsequently dissolved in the minimum amount of pentane at room temperature (ca. 100 ml) and filtered. The orange filtrate was slowly evaporated until about 3 ml of solution remained. This was cooled to –50° and worked up, as above, to give 0.35 g (43%) of shiny orange plates (m.p. 47–48° with decomp. for the freshly recrystallized compound). (Found: C, 23.11; H, 1.10. $C_8H_5HgO_6V$ calcd.: C, 21.42; H, 1.12%.)

The above analysis was performed on a sample which had been stored at –15° for approximately one week. During this storage significant amounts of dark discolored areas formed in the crystals. The product can be sublimed with partial decomposition at room temperature (0.05 mm) onto a dry ice/isopropanol cooled probe.

(Ethylmercury)pentacarbonyl(triphenylphosphine)vanadium, $C_2H_5HgV(CO)_5(C_6H_5)_3P$

A mixture of 0.20 g (0.34 mmole) of $[(C_2H_5)_4N][V(CO)_5(C_6H_5)_3P]$ and 0.091 g (0.34 mmole) of C_2H_5HgCl was dissolved with stirring in 15 ml of ice-cold methylene chloride. No reaction occured until water (15 ml) was added. After 1 h of stirring at 0° all of the $[V(CO)_5(C_6H_5)_3P]^{-1}$ had disappeared. In contrast to the corresponding preparation of $C_2H_5HgV(CO)_6$, little evidence for decomposition was observed. The work-up was identical to that described above for $(C_6H_5)_3PAuNb(CO)_6$. The overall yield after a recrystallization from methylene chloride/heptane was 0.067 g (29%) of orange needles (dec. 70–72°). The substance darkened significantly while at room temperature under nitrogen during 24 h. Attempts to obtain acceptable analyses on this substance were not successful due to its thermal instability. (Found: C, 41.66; H, 3.01. $C_{25}H_{20}HgO_5PV$ calcd.: C, 43.97; H, 2.93%.)

It was also possible to obtain $C_2H_5HgV(CO)_5(C_6H_5)_3P$ in low yield from reacting an equivalent of $(C_6H_5)_3P$ and $C_2H_5HgV(CO)_6$ in methylene chloride for 48 h at room temperature. Under these conditions most of the $C_2H_5HgV(CO)_6$ decomposes before undergoing substitution. Additional support for this formulation of the product is gained from the observation that it undergoes complete heterolytic cleavage in the presence of an equivalent of $(C_2H_5)_4NCl$ in methylene chloride to form $[V(CO)_5(C_6H_5)_3P]^{-1}$ and presumably C_2H_5HgCl.

(Ethylmercury)pentacarbonyl(triphenylphosphine)tantalum, $C_2H_5HgTa(CO)_5(C_6H_5)_3P$*, and (ethylmercury)pentacarbonyl(triphenylphosphine)niobium,* $C_2H_5HgNb(CO)_5(C_6H_5)_3P$

These thermally unstable substances were obtained from the interaction of equimolar amounts of $[(C_2H_5)_4N][M(CO)_5(C_6H_5)_3P]$, (M=Nb, Ta) and C_2H_5HgCl in methylene chloride. The preparations were carried out in exactly the same manner as that given for $(C_6H_5)_3PAuNb(CO)_6$ Only the orange-red crystalline tantalum product was isolated (19% yield, m.p. 69–71° with decomp.) and because of its poor thermal instability no attempts were made to obtain elemental analyses for it.

The infrared solution spectra of $C_2H_5HgM(CO)_5(C_6H_5)_3P$ (M=Nb, Ta) are very similar to that of the corresponding vanadium product. The solubility properties of these compounds resemble those of $(C_6H_5)_3SnV(CO)_5(C_4H_9)_3P$.

RESULTS AND DISCUSSION

Triphenyltin complexes

The unsubstituted hexacarbonyl metallate anions of niobium and tantalum are considerably more reactive toward chlorotriphenylstannane than the corresponding anion of vanadium. Although $[K(diglyme)_3][Ta(CO)_6]$ reacts readily with $(C_6H_5)_3SnCl$ in methylene chloride to form the rather unstable seven-coordinate molecule $(C_6H_5)_3SnTa(CO)_6$, under the same conditions $[Na(diglyme)_2][V(CO)_6]$ does not react. Further, it was discovered that the $(C_6H_5)_3SnM(CO)_6$ (M=V, Nb and Ta) species undergo facile heterolytic cleavage of the Sn–M bond in the presence of weak donor solvents such as diethyl ether and THF. In the latter solvent, for example, $(C_6H_5)_3SnTa(CO)_6$ completely dissociates forming the $[Ta(CO)_6]^{-1}$ anion and presumably a solvated $(C_6H_5)_3Sn^+$ species. The reaction is, however, reversible; by removing the solvent $(C_6H_5)_3SnTa(CO)_6$ is quantitatively reformed.

Many of the seven-coordinate species can be prepared only if donor molecules or other nucleophiles are removed during the reaction. The addition of water to the immiscible organic phase such as benzene or methylene chloride which contains the reactants has proved to be of great utility in removing halide ions and interfering molecules such as diglyme. For example, shaking water with a methylene chloride solution of $[Na(diglyme)_2][V(CO)_6]$ and chlorotriphenylstannane shifts the equilibrium almost entirely to the side of the product $(C_6H_5)_3SnV(CO)_6$. The removal of the chloride ion which can effectively (see later) cleave the Sn–V bond is a significant factor in promoting the formation of the product. However, the influence of the heats of solvation of the sodium cation and diglyme in water on the position of the equilibrium is also important. It was found that addition of water to a methylene chloride solution of $[(C_2H_5)_4N][V(CO)_6]$ and $(C_6H_5)_3SnCl$ does not result in the formation of $(C_6H_5)_3SnV(CO)_6$. Evidently the heat of solution of the tetraethylammonium ion in water is insufficient to shift the equilibrium to the side of the product. Thus, in planning synthesis of compounds containing metal–metal bonds from the reaction of metallates with covalent metal halides, the cation can be as important a variable as the solvent system, work-up procedure, etc.; this apparently has not always been appreciated[9].

Although there is no obvious reaction between $[Na(diglyme)_2][V(CO)_6]$ and $(C_6H_5)_3SnCl$ in dry methylene chloride after two weeks at room temperature (the reactants can be recovered essentially quantitatively at this time), an infrared spectrum of a concentrated solution (ca. 1 mmole of reactants per ml) shows a weak peak of 2075 ± 2 cm^{-1} which can be attributed to $(C_6H_5)_3SnV(CO)_6$.

The introduction of one or more phosphine ligands into the coordination sphere about the Group V metal enhances the stability of the Sn–M bond with respect to heterolytic cleavage. With vanadium, however, the direct substitution of triphenylphosphine into $(C_6H_5)_3SnV(CO)_6$ is a very slow (ca. 48 h) reaction which is accompanied by much decomposition. The substitution reactions of $(C_6H_5)_3SnTa(CO)_6$ and $(C_6H_5)_3SnNb(CO)_6$ are more facile than the corresponding vanadium complex and with both triphenylphosphine and 1,2-bis(diphenylphosphino)ethane proceed to completion within minutes at 0° in methylene chloride. Because of this rapid substitution it was possible to characterize the thermally unstable complex $(C_6H_5)_3SnNb(CO)_6$ by its reaction to give the thermally stable derivative $(C_6H_5)_3SnNb(CO)_5(C_6H_5)_3P$ and $(C_6H_5)_3SnNb(CO)_4[(C_6H_5)_2PCH_2]_2$.

It is also found that $(C_6H_5)_3SnTa(CO)_6$ reacts with triphenyl phosphite to give, after five hours, a good yield of $(C_6H_5)_3SnTa(CO)_5(C_6H_5O)_3P$. In contrast, under the same conditions triphenyl phosphite substitution into $(C_6H_5)_3SnV(CO)_6$ is not detectable even after a week.

It was found to be more convenient to synthesize the phosphine substituted derivatives by mixing chlorotriphenylstannane, the phosphine, and the appropriate hexacarbonyl metallate in methylene chloride. This reaction must proceed via the $(C_6H_5)_3SnM(CO)_6$ complexes followed by phosphine substitution rather than by phosphine substitution of the hexacarbonylmetallate and subsequent metal–metal bond formation. It has been shown previously[4] that the hexacarbonylmetallates are inert to substitution by phosphine ligands unless the reactions are performed photolytically.

The triphenylphosphine and 1,2-bis(diphenylphosphino)ethane substituted derivatives of V, Nb, and Ta have also been prepared directly from the reaction of the corresponding substituted carbonyl metallate and $(C_6H_5)_3SnCl$ in methylene chloride.

The effect of increasing substitution on the stability of the Sn–V bond to heterolytic cleavage by weak donors is quite pronounced; the order being $(C_6H_5)_3SnV(CO)_6 < (C_6H_5)_3SnV(CO)_5(C_6H_5)_3P < (C_6H_5)_3SnV(CO)_4[(C_6H_5)_2PCH_2]_2$. Complete heterolysis of $(C_6H_5)_3SnV(CO)_6$ occurs in THF whereas the other two molecules are stable in this solvent. Also $(C_6H_5)_3SnV(CO)_5(C_6H_5)_3P$ is completely dissociated in acetone, but $(C_6H_5)_3SnV(CO)_4[(C_6H_5)_2PCH_2]_2$ may be refluxed in this solvent without change. The latter compound is even sufficiently stable to heterolysis to remain unchanged in refluxing acetonitrile. The triphenyltin derivatives of niobium and tantalum complexes are less suceptible to heterolytic cleavage than the correponding vanadium ones. For example, the addition of one equivalent of tetraethylammonium chloride to a methylene chloride solution of $(C_6H_5)_3SnV(CO)_5(C_6H_5)_3P$ produces the $[V(CO)_5(C_6H_5)_3P]^{-1}$ ion quantitatively, whereas under the same conditions $(C_6H_5)_3SnTa(CO)_5(C_6H_5)_3P$ was essentially unchanged. However, the addition of a large excess, 5 equivalents, of $(C_2H_5)_4NCl$ caused the reaction to go to completion.

Similar heterolytic cleavage reactions have been reported for main group metal derivatives of other carbonylmetallates[8], the behavior of $(C_6H_5)_3SnCo(CO)_4$ is particularly relevant in this respect. In acetonitrile very little cleavage was apparent but in *N*,*N*-dimethylformamide it was essentially complete[8]. Thus, it appears that the relative tendency for triphenyltin derivatives to undergo heterolytic cleavage is $Co(CO)_4 \ll Ta(CO)_6 \approx Nb(CO)_6 < V(CO)_6$.

Triphenylphosphine gold complexes

The compounds $(C_6H_5)_3PAuM(CO)_6$ (M=V, Nb and Ta) are sufficiently more stable to heterolysis of the metal–metal bond than the corresponding triphenyltin derivatives such that they can be prepared in THF from $[Na(diglyme)_2][V(CO)_6]$ and $[K(diglyme)_3][M(CO)_6]$ (M=Nb, Ta). The cation can still be important in the synthesis, however, since $[(C_2H_5)_4N][V(CO)_6]$ only reacts with $(C_6H_5)_3PAuCl$ in methylene chloride in the presence of water. The only previously known members of the series[2] $(C_6H_5)_3PAu(CO)_6$, can also be prepared quantitatively from $(C_6H_5)_3PAuCl$ and $(C_6H_5)_3SnV(CO)_6$ in methylene chloride. Similar exchange reactions have been reported earlier for $(CH_3)_3SnCo(CO)_4$[10]. The thermal and oxidative stabilities of these complexes are also greater than those of the triphenyltin derivatives. The niobium complex $(C_6H_5)_3PAuNb(CO)_6$ like $(C_6H_5)_3SnNb(CO)_6$ is much less stable in solution than the corresponding vanadium and tantalum species. However, the crystalline $(C_6H_5)_3PAuNb(CO)_6$ was found to be as thermally and oxidatively stable as the tantalum complex. The triphenylphosphine derivatives, $(C_6H_5)_3PAuM(CO)_5(C_6H_5)_3P$ (M=V, Nb, Ta) can be prepared from the reaction of $[(C_2H_5)_4N][M(CO)_5(C_6H_5)_3P]$ with $(C_6H_5)_3PAuCl$ in methylene chloride. However, attempts to prepare these by triphenylphosphine substitution of $(C_6H_5)_3PAuM(CO)_6$ resulted instead in heterolytic cleavage of the gold–metal bond. Such behavior has not been previously noted for gold derivatives of other metal carbonyl anions, although these compounds have been studied extensively[11,12]. Addition of five equivalents of triphenylphosphine to a methylene chloride solution of $(C_6H_5)_3PAuTa(CO)_6$ causes almost immediate cleavage of all but traces of this complex. From this solution an ionic substance $\{[(C_6H_5)_3P]_3Au\}[Ta(CO)_6]$, can be isolated in good yield. The same material can be prepared from the metathesis of $\{[(C_6H_5)_3P]_4Au\}[ClO_4]$ with $[K(diglyme)_3][Ta(CO)_6]$ in acetone followed by recrystallization of the resulting solid from acetone/ethanol. The initial solid loses triphenylphosphine on recrystallization and is undoubtedly $[((C_6H_5)_3P)_4Au][Ta(CO)_6]$. A similar lability of phosphine ligands has been observed for the related d^{10} systems, $\{[(C_6H_5)_3P]_nAu\}[NO_3]$[5] where $n=2$ or 3 and $[(C_6H_5)_3P]_nPt$[13] where $n=3$ or 4.

Heterolytic cleavage of $(C_6H_5)_3PAuM(CO)_5(C_6H_5)_3P$ (M=V, Nb, Ta) by $(C_6H_5)_3P$ also occurs in methylene chloride to form $\{[(C_6H_5)_3P]_nAu\}[M(CO)_5(C_6H_5)_3P]$, but this is a much less facile process than the corresponding cleavage reaction of $(C_6H_5)_3PAuM(CO)_6$. For example, even when 24 equivalents of triphenylphosphine are added to a methylene chloride solution of $(C_6H_5)_3PAuV(CO)_5(C_6H_5)_3P$, the infrared solution spectrum indicates that there is still a significant amount of undissociated reactant present. We also have shown that this reaction rapidly attains equilibrium by obtaining the same distribution of products either by adding 3 equivalents of triphenylphosphine to one equivalent of $(C_6H_5)_3PAuV(CO)_5(C_6H_5)_3P$ or by reacting equimolar amounts of $\{[(C_6H_5)_3P]_4Au\}[ClO_4]$ and $[(C_2H_5)_4N][V(CO)_5(C_6H_5)_3P]$ in methylene chloride.

The addition of soluble halide, such as $(C_2H_5)_4NBr$, to methylene chloride solutions of $(C_6H_5)_3PAuM(CO)_6$ and $(C_6H_5)_3PAuM(CO)_5(C_6H_5)_3P$ (M=V, Nb, Ta) is more effective than triphenylphosphine on an equivalent basis in causing heterolytic cleavage of the gold–metal bond. Whereas 6 equivalents of triphenylphosphine must be added to cause complete heterolysis of $(C_6H_5)_3PAuV(CO)_6$ in methylene chloride, only one equivalent of $(C_2H_5)_4NBr$ is required to produce the same result. Most of the $(C_6H_5)_3PAuV(CO)_6$ could be reformed in the latter example by shaking the resulting solution with water. This is in accord with the earlier observation that water must be added to promote formation of $(C_6H_5)_3PAuV(CO)_6$ from a mixture of $[(C_2H_5)_4N][V(CO)_6]$ and $(C_6H_5)_3PAuCl$ in methylene chloride. The phosphine substituted species, as expected, are more difficult to cleave. For example, at least three equivalents of $(C_2H_5)_4NBr$ must be added to $(C_6H_5)_3PAuV(CO)_5(C_6H_5)_3P$ to cause all but traces of the reactant to disappear.

Ethylmercury complexes

The principle reason for preparing these substances was to compare the properties of $C_2H_5HgV(CO)_6$ and $C_2H_5HgNb(CO)_6$ with those of $C_2H_5HgTa(CO)_6$. The latter compound and the less stable $RHgTa(CO)_6$, ($R=CH_3$, C_6H_5) were the only reported seven-coordinate derivatives of $[Ta(CO)_6]^{-1}$ prior to this study[3]. Surprisingly few alkylmercury derivatives of metal carbonyl anions are known. A methylmercury derivative of $[CO(CO)_4]^{-1}$, $CH_3HgCO(CO)_4$, has been reported but it is formulated only on the basis of an infrared spectrum[14]. Unsuccessful attempts to isolate (arylmercury)tetracarbonylcobalt compounds have been noted[15]. Other than the tantalum

TABLE 1

INFRARED SOLUTION AND MULL SPECTRA OF THE TRIPHENYLTIN COMPLEXES IN THE CARBONYL REGION

Complex	Medium	C–O stretching frequencies (cm^{-1})
$Ph_3SnV(CO)_6$	cyclo-C_6H_{12}	2067 vs, 2012 m, 1987 s, 1958 vs, 1932 vs
	CH_2Cl_2	2075 vs, 2000 m(sh), 1960 vs, 1935 vs(b)
	Nujol mull	2070 s, 2015 w(sh), 1990 m, 1960 s, 1937 vs
$Ph_3SnNb(CO)_6$	CH_2Cl_2	2082 s, 2018 w, 1958 s(sh), 1940 vs
$Ph_3SnTa(CO)_6$	cyclo-C_6H_{12}	2075 vs, 2005 m(sh), 1985 s, 1960 s(sh), 1945 vs
	CH_2Cl_2	2080 s, 1954 s(sh), 1939 vs
	Nujol mull	2080 s, 2020 m, 1995 s, 1900 vs(b)
$Ph_3SnV(CO)_5PPh_3$	CH_2Cl_2	2030 s, 1970 m, 1920 vs(sh), 1902 vs, 1878 s
	Nujol mull	2030 s, 1980 m, 1927 s, 1900 vs, 1870 vs
$Ph_3SnNb(CO)_5PPh_3$	CH_2Cl_2	2050 s, 1977 m, 1929 vs, 1885 s
	Nujol mull	2045 s, 1990 m, 1936 s, 1916 vs, 1885 vs
$Ph_3SnTa(CO)_5PPh_4$	CH_2Cl_2	2045 s, 1970 m, 1925 vs, 1887 s
	Nujol mull	2040 s, 1982 m, 1927 s, 1909 vs, 1882 vs
$Ph_3SnV(CO)_4(Ph_2FCH_2)_2$	CH_2Cl_2	1972 m, 1880 vs(sh), 1865 vs(b)
	Nujol mull	1970 m, 1883 s, 1879 vs, 1850 vs
$Ph_3SnNb(CO)_4(Ph_2PCH_2)_2$	CH_2Cl_2	1989 m, 1886 vs(b)
	Nujol mull	1981 m, 1896 vs, 1872 vs, 1863 vs
$Ph_3SnTa(CO)_4(Ph_2PCH_2)_2$	CH_2Cl_2	1984 m, 1877 vs(b)
	Nujol mull	1981 m, 1885 s(sh), 1869 vs, 1858 vs(sh)
$Ph_3SnV(CO)_5PBu_3$	n-C_7H_{16}	2027 s, 1955 m, 1926 s, 1908 vs, 1892 vs
	CH_2Cl_2	2026 s, 1968 m, 1920 vs(b), 1875 vs
	Nujol mull	2020 s, 1950 s, 1920 vs, 1905 vs, 1867 vs
$Ph_3SnTa(CO)_5P(OPh)_3$	cyclo-C_6H_{12}	2050 s, 1974 m, 1939 vs, 1918 vs
	CH_2Cl_2	2045 s, 1975 m(sh), 1936 vs(b)
	Nujol mull	2055 s, 1992 m, 1924 vs, 1905 vs, 1886 vs

compounds mentioned above, it appears that the only previously well-characterized alkylmercury derivative is *cis*-$(CH_3Hg)_2Fe(CO)_4$[16,17].

We have found that $C_2H_5HgNb(CO)_6$ is virtually identical in its properties to the corresponding tantalum complex. These are discussed in the experimental section. The vanadium compound, however, is far less thermally stable as a solid. The poor analysis obtained for this substance reflects more upon its thermal instability than its initial purity since reproducible sharp melting points were obtained from freshly recrystallized samples. The close similarity in nujol mull and solution infrared spectra of this substance and $C_2H_5HgM(CO)_6$ (M = Nb, Ta) leaves little doubt as to the correctness of its formulation. The stability of these compounds to heterolytic cleavage appears to be similar to that of $(C_6H_5)_3PAuM(CO)_6$ (M = V, Nb Ta). For example, $C_2H_5HgV(CO)_6$ is completely cleaved in methylene chloride by an equivalent of $(C_2H_5)_4NBr$ to $[(C_2H_5)_4N][V(CO)_6]$ and C_2H_5HgBr.

All attempts to isolate $C_6H_5HgV(CO)_6$ were unsuccessful. The interaction of an equimolar mixture of $[Na(diglyme)_2][V(CO)_6]$ and C_6H_5HgCl in cold (−50°) methylene chloride gave a deep red solution. But on warming it above −20° extensive deposition of mercury occurred. Infrared solution spectra taken after the decompo-

TABLE 2

INFRARED SOLUTION AND MULL SPECTRA OF THE (TRIPHENYLPHOSPHINE)GOLD COMPLEXES IN THE CARBONYL REGION

Complex	Medium	C–O stretching frequencies (cm^{-1})
$Ph_3PAuV(CO)_6$	cyclo-C_6H_{12}	2042 vs, 1988 m, 1958 m, 1922 s, 1888 m(sh), 1870 m
	CH_2Cl_2	2046 vs, 1975 m, 1951 m, 1912 vs, 1856 s
	Nujol mull	2040 s, 1980 s, 1900 s(sh), 1863 vs(b)
$Ph_3PAuNb(CO)_6$	cyclo-C_6H_{12}	2055 vs, 1992 m, 1964 m, 1930 s, 1900 m(sh), 1870 m(sh)
	CH_2Cl_2	2060 vs, 1993 m, 1958 m, 1918 vs
	Nujol mull	2050 s, 1988 s, 1879 vs(b)
$Ph_3PAuTa(CO)_6$	cyclo-C_6H_{12}	2055 vs, 1985 m, 1955 m, 1920 s, 1900 m(bsh)
	CH_2Cl_2	2050 s, 1985 m, 1950 s, 1915 vs
	Nujol mull	2050 s, 1975 s, 1875 vs(b)
$Ph_3PAuV(CO)_5PPh_3$	cyclo-C_6H_{12}	1995 s, 1924 m, 1885 vs, 1875 vs(sh), 1819 s
	CH_2Cl_2	1995 s, 1922 s, 1875 vs, 1810 s
	Nujol mull	1993 s, 1928 m(sh), 1915 s, 1880 vs, 1792 vs
$Ph_3PAuNb(CO)_5PPh_3$	cyclo-C_6H_{12}	2014 s, 1938 s, 1896 vs, 1879 vs(sh) 1829 s
	CH_2Cl_2	2012 s, 1931 s(sh), 1889 vs, 1815 s
	Nujol mull	2005 s, 1945 m(sh), 1924 s, 1889 vs(b), 1800 vs
$Ph_3PAuTa(CO)_5PPh_3$	cyclo-C_6H_{12}	2005 s, 1928 s, 1886 vs, 1876 vs(sh), 1829 s
	CH_2Cl_2	2005 s, 1918 s, 1878 vs, 1818 s
	Nujol mull	2002 s, 1930 m(sh), 1915 s, 1880 vs(b), 1802 vs
$[(Ph_3P)_3Au][Ta(CO)_6]$	CH_2Cl_2	1850 vs
	Nujol mull	1869 s, 1848 vs

TABLE 3

INFRARED SOLUTION AND MULL SPECTRA OF THE ETHYLMERCURY COMPLEXES IN THE CARBONYL REGION

Complex	Medium	C–O stretching frequencies (cm^{-1})
$EtHgV(CO)_6$	cyclo-C_6H_{12}	2065 vs, 2005 w, 1995 m, 1950 s, 1918 s
	CH_2Cl_2	2060 s, 1995 m(sh), 1965 m(sh), 1940 vs, 1905 s
	Nujol mull	2060 vs, 2007 m, 1977 m, 1945 s, 1915 s
$EtHgNb(CO)_6$	cyclo-C_6H_{12}	2073 s, 2006 m(sh), 1993 m, 1949 s, 1931 s
	CH_2Cl_2	2072 s, 2000 m, 1934 s
	Nujol mull	2070 s, 2006 m, 1995 m, 1948 s, 1929 vs
$EtHgTa(CO)_6$	cyclo-C_6H_{12}	2070 vs, 2000 m(sh), 1991 m, 1944 s, 1927 vs
	CH_2Cl_2	2070 s, 1990 m(sh), 1972 m, 1935 vs(b)
	Nujoll mull	2070 s, 1997 m, 1982 m, 1940 s, 1925 vs
$EtHgV(CO)_5PPh_3$	cyclo-C_6H_{12}	2018 s, 1963 m(sh), 1932 s(sh), 1905 vs, 1860 vs
	CH_2Cl_2	2016 m, 1940 m(sh), 1898 vs, 1848 s
	Nujol mull	2015 s, 1950 s, 1885 vs(b), 1836 s
$EtHgNb(CO)_5PPh_3$	CH_2Cl_2	2025 s, 1949 m, 1904 vs, 1880 s(bsh)
$EtHgTa(CO)_5PPh_3$	cyclo-C_6H_{12}	2025 m, 1946 m, 1910 vs, 1874 s
	CH_2Cl_2	2025 m, 1940 m(sh), 1905 vs, 1860 s
	Nujol mull	2030 s, 1955 s, 1928 s, 1891 vs, 1858 vs

sition showed $V(CO)_6$ and $[V(CO)_6]^{-1}$ to be the principle carbonyl containing species present.

Unfortunately, the thermal stabilities of the crystalline triphenylphosphine substituted products, $C_2H_5HgM(CO)_5(C_6H_5)_3P$, (M=V, Nb, Ta) are no better than those of the corresponding unsubstituted products. In solution the substituted niobium and tantalum complexes appear to be even less thermally stable than $C_2H_5HgM(CO)_6$ (M=Nb, Ta). Accordingly, the compounds give poor analyses. In the case of $C_2H_5HgV(CO)_5(C_6H_5)_3P$, however, the formulation is supported on the basis of its preparation by two independent routes; *i.e.* it was prepared by the reaction of C_2H_5HgCl and $[V(CO)_5(C_6H_5)_3P]^{-1}$ and the substitution of $(C_6H_5)_3P$ into $C_2H_5HgV(CO)_6$. Also, heterolytic cleavage of this substance by $(C_2H_5)_4NCl$ gives only $[V(CO)_5(C_6H_5)_3P]^{-1}$ as the carbonyl containing product.

Infrared spectra

For a given class of compounds, *e.g.* $(C_6H_5)_3SnM(CO)_5L$ or $C_2H_5HgM(CO)_6$ (M=V, Nb, Ta), the positions, shapes and relative intensities of the bands found in their solution or mull infrared spectra in the carbonyl stretching frequency are very similar; for corresponding niobium and tantalum compounds the spectra in this region are nearly superimposable. The vanadium compounds invariably absorb at lower energy than the analogous niobium and tantalum ones.

It is highly likely that the structures of corresponding vanadium, niobium and tantalum compounds are similar because of the close resemblance of their infrared spectra. However, otherwise, little positive structural information can be inferred from these spectra.

REFERENCES

1 A. Davison and J. E. Ellis, *J. Organometal. Chem.*, 23 (1970) C1.
2 A. S. Kasenally, R. S. Nyholm, R. J. O'Brien and M. Stiddard, *Nature*, 204 (1964) 871.
3 K. A. Keblys and M. Dubeck, *Inorg. Chem.*, 3 (1964) 1646.
4 A. Davison and J. E. Ellis, *J. Organometal. Chem.*, 31 (1971) 239.
5 L. Malatesta, L. Naldini, G. Simonetta and F. Cariati, *Coord. Chem. Rev.*, 1 (1966) 255.
6 W. Hewerton and H. R. Watson, *J. Chem. Soc.*, (1962) 1490.
7 R. P. M. Werner and H. E. Podall, *Chem. Ind., (London)*, (1961) 144.
8 J. M. Burlitch, *J. Amer. Chem. Soc.*, 91 (1969) 4562, 4563.
9 R. E. Dessy and P. M. Weissman, *J. Amer. Chem. Soc.*, 88 (1966) 5124.
10 E. W. Abel and G. V. Hudson, *J. Inorg. Nucl. Chem.*, 30 (1969) 2339.
11 C. E. Coffey, J. Lewis and R. S. Nyholm, *J. Chem. Soc.* (1964) 1741.
12 A. S. Kasenally, J. Lewis, A. R. Manning, J. R. Miller, R. S. Nyholm and M. Stiddard, *J. Chem. Soc.*, (1965) 3407.
13 L. Malatesta and R. Ugo, *J. Chem. Soc.*, (1963) 2080.
14 O. Kahn, J. Henrion and G. Bouquet, *Bull. Soc. Chim. Fr.*, (1967) 3547.
15 D. Seyferth and R. J. Spohn, *J. Amer. Chem. Soc.*, 91 (1969) 3037, 6192.
16 Z. Hein and E. Heuser, *Z. Anorg. Allg. Chem.*, 249 (1942) 293.
17 O. Kahn and M. Bigorgne, *C.R. Acad. Sci.*, 261 (1965) 2483.