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

THE CHEMISTRY OF THE GROUP V METAL CARBONYLS
III. THE PREPARATION OF SUBSTITUTED CARBONYL ANIONS OF VANADIUM, NIOBIUM AND TANTALUM*

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(Received March 15th, 1971)

SUMMARY

The first practical route to substituted carbonyl anions of niobium and tantalum, involving the photolytically induced substitution of mono- and bidentate phosphines into the hexacarbonylmetallate(−I) anions of these metals, has been utilized in obtaining $[(C_2H_5)_4N][M(CO)_5P(C_6H_5)_3]$ and $[(C_2H_5)_4N][M(CO)_4(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$ (M = Nb, Ta). This new pathway also represents the best available method for preparing phosphine, arsine, and stibene substituted carbonyl anions of vanadium; tetraethylammonium salts of $[V(CO)_5L]^-$, where L represents $(C_6H_5)_3M$ (M = P, As, Sb), or $(n\text{-}C_4H_9)_3P$ and $[V(CO)_4L']^-$, where L′ is $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ or $[(C_6H_5)_2AsC_5H_4]_2Fe$ have been obtained in high yields by this procedure.

INTRODUCTION

The general procedures available for the preparation of substituted metal carbonyl anions have involved reduction of the corresponding metal carbonyl[2,3], metal carbonyl halide[4] or hydride and substitution of halides and other anionic species, including metal carbonyl anions, *into* neutral metal carbonyls[3,5,6].

Other less general routes to such species include Lewis base induced disproportionation of metal carbonyls[7], a process which generally results in the formation of unsubstituted metal carbonyl anions[2,3], halogen oxidation of certain neutral phosphine carbonyls[8], and substitution of free ligands into metal carbonyl anions on mixing or heating in solution. In principle, the latter method should be the most direct way of making substituted anions and a few preparations based on it have been reported[6,9,10] but this procedure has been of little general synthetic value[2,11]. For example, we have found that the hexacarbonylmetallate anions of group Va remain unchanged in molten triphenylphosphine.

Although the substitution of ligands into neutral metal carbonyls and cationic carbonyl species via photolysis has been a recognized procedure for many years, to

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* For Part II see ref. 1.

** NSF Traineeship 1970–1971.

our knowledge no analogous substitution of donor molecules *into* metal carbonyl anions has appeared in the literature[2,3,12].

Accordingly, we now report on the first direct substitution of donor molecules into the coordination sphere of metal carbonyl anions via photolysis. This new synthetic pathway for the preparation of substituted metal carbonyl anions promises to be of general importance, particularly when the corresponding neutral metal carbonyl, metal carbonyl halide or hydride does not exist or is of marginal stability. Although we have reported[13] the first synthesis of $[(C_6H_5)_3PM(CO)_5]^-$ (M = Nb and Ta) in low yields (ca. 1 %), the photolytic procedure represents the only practical route to substituted carbonyl anions of these metals. It also gives much improved yields of vanadium derivatives made by other methods[7,13].

EXPERIMENTAL

General procedures and starting materials

All operations were carried out under an atmosphere of purified nitrogen further purified by passage through a column of activated copper catalyst[14]. Solutions were transferred by stainless steel cannulae and syringes; otherwise reactions were worked up using standard Schlenck technique[15]. Medium porosity sintered glass discs were used for filtrations, except where noted. The reactants and products were routinely handled in subdued light and stored in the dark.

Reagent grade ethanol, n-butanol and acetone were freed of oxygen by purging with a dispersed stream of nitrogen; distilled water was treated similarly. Tetrahydrofuran (THF), benzene and diethyl ether were freshly distilled from the benzophenone ketyls of sodium, potassium and sodium/potassium (NaK_2), respectively. Pentane and hexane were dried over and distilled from sodium potassium alloy (NaK_2) and potassium, respectively, and subsequently purged with nitrogen before use.

Bis(diglyme)sodium hexacarbonylvanadate(−I) and the tetraalkylammonium hexacarbonylmetallates(−I) were prepared using published procedures[16]. Ferrocene-1,1′-bis(diphenylarsine), (FDPA), was prepared by Dr. J. J. Bishop[17]. The triphenylpnictines (M = P, As, Sb) and 1,2-bis(diphenylphosphino)ethane were obtained from commercial sources and recrystallized from ethanol before use. Tri-n-butylphosphine was obtained from a commercial source and used without purification.

IR spectra were recorded on a Perkin–Elmer Model 237B 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.

Photolyses were conducted in a borosilicate reaction vessel of about 150 ml capacity, similar to Ace Glass Model 6515. A high pressure Hanovia quartz mercury vapor lamp (450 watts, Model 679A-36) inside a water cooled quartz photochemical immersion well (Ace Glass Model 6515-25) was the light source. The reactions proceeded in a magnetically stirred solution at room temperature, with exceptions noted. All solvent evaporations and drying operations were done *in vacuo*, at or below room temperature. The photolyses were monitored by the decline in intensity of the carbonyl stretching frequency absorption at 1860 cm^{-1}, due to the hexacarbonylmetallate anions. When this band became very weak or disappeared, the photolyses were stopped. In contrast to the substituted anions of vanadium, those of niobium and tantalum are easily decomposed by long exposures to UV radiation and thus their formations were carefully monitored.

Tetraethylammonium tetracarbonyl[1,2-bis(diphenylphosphino)ethane]vanadate(−I), $[(C_2H_5)_4N]\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}$

A light yellow solution of 5.0 g (9.8 mmol) of bis(diglyme)sodium hexacarbonylvanadate(−I) and 6.0 g (15.0 mmol) of 1,2-bis(diphenylphosphino)ethane in 120 ml of THF was photolyzed for 10.5 h. The solvent was evaporated from the deep red solution leaving an oil which partly solidified overnight. This oil completely solidified after extensive trituration and washing with light petroleum ether and was dried. The resulting crude orange red sodium salt (pyrophoric!) was next converted to the more tractable tetraethylammonium salt. It was dissolved in the minimum amount of ethanol (600 ml) and filtered to give a clear blood red solution. The addition of 4.0 g (19 mmol) of tetraethylammonium bromide in 50 ml ethanol to the filtrate resulted in immediate precipitation of an orange red solid. After evaporation of all but 100 ml of ethanol, water (300 ml) was added: the solution became turbid and more orange red solid formed. The mixture was filtered through a coarse porosity sintered glass disc: the resulting solid was washed with water (3 × 50 ml), dried, and dissolved in the minimum amount (ca. 340 ml) of acetone/n-butanol solvent mixture (16/1, v/v). Upon slow evaporation of solvent from the filtrate red needles formed. When all but ca. 20 ml of solvent had evaporated the supernatant liquor was removed. The crystals were then washed with benzene (2 × 10 ml) to remove any free phosphine and subsequently treated with pentane until the washings were colorless. The first crop of crystals were recrystallized from acetone/n-butanol to give 2.80 g (42% yield) of analytically pure product. The orange-red crystalline material can be handled in air for brief periods without noticeable change. It is slightly soluble in methylene chloride, acetone and THF, poorly soluble in benzene and ethanol, and insoluble in saturated hydrocarbons, diethyl ether, n-butanol and water. Methylene chloride solutions of this anion (and those of the other anions mentioned in this paper) deteriorate rapidly at room temperature.

Tetraethylammonium tetracarbonyl[1,2-bis(diphenylphosphino)ethane]niobate(−I) and -tantalate(−I), $[(C_2H_5)_4N]\{Nb(CO)_4[(C_6H_5)_2PCH_2]_2\}$ *and* $[(C_2H_5)_4N]\{Ta(CO)_4[(C_6H_5)_2PCH_2]_2\}$

These species were prepared and isolated by the same procedure used for the corresponding vanadium salt except that the tetraethylammonium salts of the hexacarbonylmetallates of niobium and tantalum were used to avoid the metathesis step outlined above.

The photolyses were performed with ca. 4 mmol of anion and 6 mmol of the phosphine in 130 ml THF and were usually stopped after 5–10 h. During the reaction period crystalline product often separated from solution as red needles. Such crystallization did not usually hinder the progress of the reaction, but occasionally it was necessary to clean the quartz probe of crystals and decomposition material to allow the photolysis to proceed smoothly. The red niobium and deep red tantalum salts, obtained in 50–60% yield, have qualitatively the same solubility properties as the vanadium salt. However, they are more air sensitive than the vanadium salt and slowly change to white powders in air.

Tetraethylammonium (triphenylarsine)pentacarbonylvanadate(−I), $[(C_2H_5)_4N][V(CO)_5As(C_6H_5)_3]$

A mixture of 3.9 g (7.6 mmol) of $[Na(diglyme)_2][V(CO)_6]$ and 7.0 g (23 mmol) of triphenylarsine were dissolved in THF (130 ml) and the resulting solution was photolyzed for 11 h. The deep orange brown solution was worked up by the same method as outlined in the preceding vanadium photolysis to give a crude tetraethylammonium salt. This was dissolved in the minimum amount of acetone (600 ml) and filtered. The solvent was evaporated until ca. 10 ml of solution remained. The addition of diethyl ether (150 ml) to this solution caused an immediate formation of deep yellow crystals. They were filtered, washed with diethyl ether (20 ml), pentane (20 ml) and dried. This recrystallization was sufficient to provide a sample free of reactants. A second recrystallization from acetone/diethyl ether provided 3.37 g (70% yield) of analytically pure product. Bright yellow $[(C_2H_5)_4N][V(CO)_5P(C_6H_5)_3]$ and golden $[(C_2H_5)_4N][V(CO)_5Sb(C_6H_5)_3]$ were prepared by identical procedures in 65% and 75% yields, respectively. These salts all have qualitatively the same solubility properties. They are insoluble in saturated hydrocarbons, diethyl ether, ethyl acetate and water, very slightly soluble in aromatic hydrocarbons and alcohols and soluble in acetone, THF, methylene chloride and dimethylformamide.

Tetraethylammonium(triphenylphosphine)pentacarbonylniobate(−I), $[(C_2H_5)_4N][Nb(CO)_5P(C_6H_5)_3]$

An orange yellow solution of 2.66 g (6.8 mmol) of tetraethylammonium hexacarbonylniobate(−I) and 5.35 g (20.4 mmol) of triphenylphosphine in THF (130 ml) was photolyzed for 6 h. In contrast to the corresponding vanadium preparation, it was necessary to run this reaction at 40–60° to allow it to proceed at a reasonable rate. Careful monitoring was essential to prevent excessive decomposition of the product by prolonged photolysis; *e.g.*, a reaction was allowed to proceed overnight at room temperature and nearly complete decomposition of the product resulted. The work up was analogous to that of the corresponding vanadium compound.

The first recrystallization from acetone/diethyl ether gave 2.77 g (65% yield) of orange plates, free of $[(C_2H_5)_4N][Nb(CO)_6]$. It was necessary to recrystallize the above product twice to obtain an analytically pure sample. Red orange $[(C_2H_5)_4N][Ta(CO)_5P(C_6H_5)_3]$ was prepared by the same procedure: however, it may be more prone to photolytic decomposition than the niobium species as it could be obtained in only 35–40% yields. The solubility properties of these species are qualitatively the same as those for $[(C_2H_5)_4N][V(CO)_5P(C_6H_5)_3]$.

*Tetraethylammonium tetracarbonyl[ferrocene-*1,1′*-bis(diphenylarsine)]vanadate(−I),* $[(C_2H_5)_4N]\{V(CO)_4[(C_6H_5)_2AsC_5H_4]_2Fe)\}$

A solution of 2.25 g (6.45 mmol) of tetraethylammonium hexacarbonylvanadate(−I) and 6.2 g (9.67 mmol) of ferrocene-1,1′-bis(diphenylarsine) in THF (130 ml) was photolyzed for 20 h. The crude solid, obtained from evaporation of the solution, was extracted for 24 h with refluxing hexane to remove free arsine (recovery: 2.45 g); the remaining solid was recrystallized from an acetone/n-butanol (30/1, v/v) solvent mixture (155 ml). Slow evaporation of solvent was necessary to prevent the product from oiling. When ca. 15 ml of solution remained the solid was separated from the supernatant liquor, washed with pentane until the washings were colorless, and dried. A second recrystallization from acetone/n-butanol gave 3.12 g (52% yield) of analytically pure, red orange, crystalline product. The salt is insoluble in saturated hydrocarbons, diethyl ether, alcohols and water, slightly soluble in hot aromatic hydrocarbons and ethyl acetate and soluble in acetone, THF, dimethylformamide and dimethyl sulfoxide.

Tetraethylammonium(tri-n-butylphosphine)pentacarbonylvanadate(−I), $[(C_2H_5)_4N][V(CO)_5P(C_4H_9)_3]$

After 7 h the photolysis of a solution which originally contained 1.75 g (5.0 mmol) of tetraethylammonium hexacarbonylvanadate(−I) and 3.0 g (15.0 mmol) of tri-n-butylphosphine in THF (130 ml) was stopped. The yellow brown solution was filtered and the filtrate was evaporated to a viscous deep brown oil at 30–40°. The oil solidified upon trituration and washing with pentane to give an air sensitive yellow-green solid, which smelled strongly of free phosphine. This was dissolved in a minimum amount of diethyl ether (30 ml) and filtered. The filtrate was cooled to −20°, whereupon fine fibrous yellow crystals came out of solution. This crystalline slurry was filtered at −20°, washed with cold diethyl ether (20 ml at −40°), pentane (20 ml at room temp.) and then dried. The resulting bright yellow needles (1.8 g: 68% yield) still smelled slightly of free phosphine but were less air sensitive. Although the above product was free of other carbonyl containing impurities, two additional recrystallizations at −20° from diethyl ethyl were necessary to give an analytically pure sample. The solid and its solutions are significantly more air sensitive than those of the other substituted vanadium carbonyl anions. Also, unlike the other salts, this compound is fairly soluble in aromatic hydrocarbons, alcohols, diglyme and diethyl ether. It is insoluble in water and saturated hydrocarbons, but soluble in most other organic solvents.

RESULTS AND DISCUSSION

Vanadium compounds

We have found that triphenyl pnictines (M = P, As, Sb) and tri-n-butylphosphine substituted hexacarbonylvanadates(−I), under photolytic conditions, to give monosubstituted pentacarbonylvanadate(−I) ions in 65–75% yields. The only compound of the above series previously known, the triphenylphosphine derivative[13], and several related salts, $[(CH_3)_4N][LV(CO)_5]$, where L represents various (2-alkenylphenyl)diphenylphosphines[11], have been prepared recently by more laborious procedures, involving reduction of appropriately substituted tetracarbonylvanadium(0) species. The tri-n-butylphosphine substituted anion is the first (trialkylphosphine)pentacarbonylvanadate(−I) anion reported, although tetracarbonylbis(trialkylphosphine)vanadium(0) compounds have been known for several years[18].

The substitution of the bidentate ligands, 1,2-bis(diphenylphosphino)ethane (Diphos), and ferrocene-1,1′-bis(diphenylarsine) (FDPA), into $[V(CO)_6]^-$ also occurs

TABLE 1

ELEMENTAL COMPOSITION AND PROPERTIES OF THE METAL CARBONYL ANIONS

Compound[a]	M.p. (°C)	Empirical formula	Analysis found (calcd.) (%) C	H	N
$[(C_2H_5)_4N][V(CO)_5P(C_6H_5)_3]$	191–193	$C_{31}H_{35}NO_5PV$	63.61 (63.80)	5.87 (6.04)	2.29 (2.40)
$[(C_2H_5)_4N][Nb(CO)_5P(C_6H_5)_3]$	158–160 dec.	$C_{31}H_{35}NNbO_5P$	59.18 (59.35)	5.96 (5.64)	2.80[b,c] (2.24)
$[(C_2H_5)_4N][Ta(CO)_5P(C_6H_5)_3]$	190–192	$C_{31}H_{35}NO_5PTa$	51.77 (52.50)	5.15 (4.94)	1.84 (1.96)
$[(C_2H_5)_4N][V(CO)_4Diphos]$	256–260 dec.	$C_{38}H_{44}NO_4P_2V$	66.36 (65.99)	6.61 (6.42)	1.88[d] (2.03)
$[(C_2H_5)_4N][Nb(CO)_4Diphos]$	204–208 dec.	$C_{38}H_{44}NNbO_4P_2$	61.74 (62.21)	6.04 (6.05)	1.69 (1.91)
$[(C_2H_5)_4N][Ta(CO)_4Diphos]$	208–212 dec.	$C_{38}H_{44}NO_4P_2Ta$	55.64 (55.55)	5.35 (5.40)	1.91 (1.71)
$[(C_2H_5)_4N][V(CO)_5As(C_6H_5)_3]$	130–133	$C_{31}H_{35}AsNO_5V$	59.23 (59.35)	5.67 (5.62)	2.12 (2.23)
$[(C_2H_5)_4N][V(CO)_5Sb(C_6H_5)_3]$	152–155	$C_{31}H_{35}NO_5SbV$	54.89 (55.22)	5.45 (5.23)	2.17 (2.08)
$[(C_2H_5)_4N][V(CO)_5P(C_4H_9)_3]$	69–71	$C_{25}H_{47}NO_5PV$	57.32 (57.35)	9.15 (9.05)	2.83 (2.68)
$[(C_2H_5)_4N][V(CO)_4FDPA]$	170–173	$C_{46}H_{48}AsFeNO_4V$	59.06 (59.06)	5.23 (5.17)	1.70 (1.50)

[a] Diphos = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, FDPA = $[(C_6H_5)_2AsC_5H_4]_2Fe$. [b] Found: P, 4.61. Calcd.: P, 4.95%. [c] $[(C_6H_5)_4As][Nb(CO)_5P(C_6H_5)_3]$, found: C, 64.03; H, 3.86; As, 8.44. $C_{47}H_{35}AsNbO_5P$ calcd.: C, 64.23; H, 4.00; As, 8.53%. [d] Found: P, 8.63. Calcd.: P, 8.97%.

readily under photolytic conditions to give tetracarbonyl-*cis*-disubstituted vanadate(−I) ions, in 40–50% yields. The Diphos derivative has been previously prepared as the tris(2,2′-bipyridyl)vanadium(II) salt by a comparatively difficult synthesis[7] involving a 2,2′-bipyridyl disproportionation of tetracarbonyl[1,2-bis(diphenylphosphino)ethane]vanadium(0). The formation of $[LV(CO)_4]^-$, where L = Diphos or FDPA, most probably proceeds via the monosubstituted intermediate $[LV(CO)_5]^-$, which contains one uncoordinated phosphine or arsine, respectively. The supernatant liquor remaining after the first crystallization of crude $[(C_2H_5)_4N][V(CO)_4Diphos]$ from acetone/n-butanol (see Experimental) contained free Diphos, the tetraethylammonium salts of $[V(CO)_6]^-$ and $[Diphos\ V(CO)_4]^-$ and a substance, (A), which had a three band pattern expected of a $[LV(CO)_5]^-$ ion in the carbonyl stretching frequency region. This substance could not be separated from free ligand. On the basis of its IR spectrum (Table 2), its solubility properties, and its reaction with $(C_6H_5)_3SnCl$ to yield $(C_6H_5)_3SnV(CO)_4Diphos$[19], (A) is formulated as $[(C_2H_5)_4N][V(CO)_5Diphos]$*. The reaction of $(C_6H_5)_3SnCl$ with (A) is presumed to proceed through a transient intermediate, $(C_6H_5)_3SnV(CO)_5Diphos$, the uncoordinated phosphine in this intermediate then rapidly displaces carbon monoxide. The observation that

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* The preparation of $Ph_3SnV(CO_4)Diphos$ from (A) excludes the alternate formulation $[(C_2H_5)_4N]_2\{[(CO)_5V]_2Diphos\}$.

TABLE 2

IR SPECTRA IN THE CARBONYL REGION

Compound[a]	Nujoll mull (cm^{-1})					THF solution (cm^{-1})			
$[(C_2H_5)_4N][V(CO)_5P(C_6H_5)_3]$	1959 m	1845 m (sh)	1810 vs	1766 s		1965 s	1858 m	1823 vs	
$[(C_2H_5)_4N][Nb(CO)_5P(C_6H_5)_3]$	1969 s	1856 s	1818 vs	1797 vs	1772 s (sh)	1971 s	1863 m	1830 vs	
$[(C_2H_5)_4N][Ta(CO)_5P(C_6H_5)_3]$	1970 s	1849 s (sh)	1821 vs (br)		1771 s	1973 s	1863 m	1828 vs	
$[(C_2H_5)_4N][V(CO)_4Diphos]$	1899 s	1781 vs	1765 vs	1724 vs		1903 s	1799 vs	1780 s	1747 m
$[(C_2H_5)_4N][V(CO)_5Diphos]$[b]	1965 s	1860 s	1800 vs (br)			1970 s	1857 mw	1824 vs	
$[(C_2H_5)_4N][Nb(CO)_4Diphos]$	1897 s	1785 s	1758 s	1738 vs		1909 s	1803 vs	1780 s	1750 m
$[(C_2H_5)_4N][Ta(CO)_4Diphos]$	1893 s	1778 s	1755 s	1736 vs		1908 s	1800 vs	1779 s	1752 m
$[(C_2H_5)_4N][V(CO)_5As(C_6H_5)_3]$	1965 m	1850 s (sh)	1820 vs (br)		1770 vs	1969 s	1859 m	1826 vs	
$[(C_2H_5)_4N][V(CO)_5Sb(C_6H_5)_3]$	1964 s	1862 m	1820 s (sh)	1809 vs (br)		1968 s	1859 m (sh)	1831 vs	
$[(C_2H_5)_4N][V(CO)_5P(C_4H_9)_3]$	1961 s	1849 s	1813 vs	1793 vs	1763 vs	1963 s	1856 m	1813 vs	
$[(C_2H_5)_4N][V(CO)_4FDPA]$	1899 s	1789 vs	1755 vs (sh)	1742 vs		1907 s	1796 vs	1780 s (sh)	1745 m

[a] Diphos = 1,2-bis(diphenylphosphino)ethane, FDPA = ferrocene-1,1'-bis(diphenyl)arsine. [b] Contaminated with free Diphos.

$(C_6H_5)_3SnV(CO)_6$ reacts with Diphos to give only $(C_6H_5)_3SnV(CO)_4$Diphos[19] is consistent with this interpretation. Although it has not been unequivocally shown that the photolysis of (A) yields $[(C_2H_5)_4N][V(CO)_4$Diphos$]$, the solution spectrum of (A) in the carbonyl stretching frequency region is superimposable with that of the intermediate observed during the photolysis of $[(C_2H_5)_4N][V(CO)_6]$ with Diphos.

Although the isoelectronic species, hexacarbonylchromium(0), under photolytic conditions readily forms THF·$Cr(CO)_5$[12] and diglyme·$Cr(CO)_3$[12], no analogous vanadium species could be detected during photolyses of $[V(CO)_6]^-$ in THF and diglyme, even though the anion slowly decomposed under these conditions. Also no reaction occurred during ca. 15 h of photolysis of $[V(CO)_6]^-$ and mesitylene*, thiophene, diphenyl sulfide or triethylamine in THF. In contrast, after about five hours of photolysis, $[V(CO)_6]^-$ in neat acetonitrile or pyridine gave a black or deep red solution, respectively. However, no new carbonyl containing species were isolated from these reactions. The photolysis of $[V(CO)_6]^-$ in the presence of triphenylphosphite or 2,2'-bipyridyl gives a product which has an IR spectrum characteristic of $[LV(CO)_5]^-$ or $[LV(CO)_4]^-$, respectively.

Niobium and tantalum compounds

The photolytically induced substitution of triphenylphosphine and 1,2-bis(diphenylphosphino)ethane into the hexacarbonylmetallate(−I) ions of niobium and tantalum provide tetraethylammonium tetracarbonyl[1,2-bis(diphenylphosphino)ethane]niobate(−I) and -tantalate(−I) in 50–55% yields. In contrast to the $[V(CO)_4$Diphos$]^-$ preparation, no monosubstituted intermediates were detected during the photolyses. Although 60–65% yields of $[(C_2H_5)_4N][Nb(CO)_5P(C_6H_5)_3]$ have been obtained, only 35–40% yields of the corresponding tantalum salt were realized. In the preparation of the latter species, unlike that of $[V(CO)_5P(C_6H_5)_3]^-$, it was necessary to run the reactions at 40–60° to allow them to proceed at a reasonable rate. The substitution of donor molecules into $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ may then be less facile than the corresponding vanadium reactions.

Infrared spectra

The THF solution spectra of the $[LM(CO)_5]^-$ ions (Table 2) show three line patterns in the carbonyl stretching frequency region expected for monosubstituted octahedral molecules. The shapes and relative intensities of the three bands are very similar for all of these salts. The stretching frequencies of (tri-n-butylphosphine)pentacarbonylvanadate(−I) ions are at somewhat lower frequencies than those of the other substituted pentacarbonylmetallates(−I); this is reasonable in view of the greater σ-donor ability of tri-n-butylphosphine compared to those of the triphenylpnictines.

The solution spectra of the $[LM(CO)_4]^-$ ions show a four line pattern expected for an octahedral *cis*-disubstituted metal tetracarbonyl species. The shape and relative intensities of the bands observed for all four salts are quite similar in both solution and mull spectra.

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* The desired product, tricarbonylmesitylenevanadate(−I), has been prepared by a less direct route[1].

ACKNOWLEDGEMENT

We wish to thank the National Science Foundation for financial support (Grants GP 6672 and GP-11001).

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