

of hexagonal phases.⁸ Low-angle X-ray scattering studies of cardiolipin-divalent cation complexes with Ca^{2+} , Mg^{2+} , and Ba^{2+} have been carried out, but unfortunately Cd^{2+} studies have not. Nevertheless, Ca^{2+} in comparison to Mg^{2+} and Ba^{2+} is found to promote a particularly small area per head group. On the basis of measured spacing between cylinders and estimated partial specific volume of the lipid, an area of 29 \AA^2 is found. The Mg^{2+} and Ba^{2+} complexes have areas of 38 and 39 \AA^2 , respectively.⁹ Preferential formation of hexagonal phases with Ca^{2+} have been explained on this basis.

The parallel rows of bridged cations found in the crystals discussed here are very reminiscent of the arrays of long aqueous channels separated by hydrophobic acyl chains that characterize lipid hexagonal phases. It is instructive, therefore, to view our structures on the basis of a surface area per phosphate at the boundaries of the ion channels. We will define a cylindrical surface passing through all phosphorus atoms. Mg, Cd, and Ba structures have cylinder diameters

of 4.6, 5.4, and 5.7 \AA and surface areas of 34, 22, and 27 \AA^2 per phosphate, respectively. The minimum area for Cd and the similarity in magnitude to values observed for the lipid phases in which Ca^{2+} rather than Cd^{2+} was studied suggest that coordination geometries found in simple phosphate complexes may extend to even complex lipid systems. Moreover, these geometries may be at the heart of Ca^{2+} and Cd^{2+} selectivity in membrane transformations. Anticipated work applying ^{113}Cd solid NMR techniques to crystalline Cd complexes and lipid dispersions should allow testing of this possibility.

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Supplementary Material Available: A table including h , k , l , F_o , and F_c for all reflections collected along with a list of anisotropic thermal parameters (11 pages). Ordering information is given on any current masthead page.

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Studies on Carbonyl Derivatives of Early Transition Elements. A Convenient Method for the Preparation of the $[\text{Nb}(\text{CO})_6]^-$ Anion at Atmospheric Pressure and Room Temperature. Crystal and Molecular Structure of $[\text{M}(\text{CO})_6]^-$ ($\text{M} = \text{Nb, Ta}$) as Their Bis(triphenylphosphine)nitrogen(1+) Derivatives

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A new method is reported for the preparation of $[\text{Nb}(\text{CO})_6]^-$ and $[\text{Ta}(\text{CO})_6]^-$ by reductive carbonylation of M_2Cl_{10} ($\text{M} = \text{Nb, Ta}$) with the magnesium-zinc-pyridine-CO system. In the case of niobium, the reductive carbonylation occurs at atmospheric pressure and room temperature with yields as high as 48%. The tetrahydrofuran-stabilized sodium derivatives $[\text{Na}(\text{THF})][\text{M}(\text{CO})_6]$ and the bis(triphenylphosphine)nitrogen(1+) derivatives, $\text{PPN}[\text{M}(\text{CO})_6]$ ($\text{M} = \text{Nb, Ta}$), are reported. The crystal and molecular structures of both niobium and tantalum $\text{PPN}[\text{M}(\text{CO})_6]$ complexes are described. Both compounds are isostructural with the corresponding vanadium derivative: rhombohedral, space group $R\bar{3}$, one molecule per cell; $\text{M} = \text{Nb}$, $a = 9.832(4) \text{ \AA}$, $\alpha = 91.98(5)^\circ$, $V = 948.7(7) \text{ \AA}^3$, $\rho_{\text{calcd}} = 1.399 \text{ g cm}^{-3}$, $R = 0.0391$; $\text{M} = \text{Ta}$, $a = 9.814(4) \text{ \AA}$, $\alpha = 92.02(8)^\circ$, $V = 943.4(7) \text{ \AA}^3$, $\rho_{\text{calcd}} = 1.562 \text{ g cm}^{-3}$, $R = 0.0294$ ($\text{Mo K}\alpha$, $\lambda = 0.71069 \text{ \AA}$). The geometry of the two hexacarbonylmetalates is that of an almost perfect octahedron. Chemical and spectroscopic comparisons of the three $[\text{M}(\text{CO})_6]^-$ ($\text{M} = \text{V, Nb, Ta}$) anions are made.

The chemistry of binary carbonyl derivatives of group 5 metals, especially of niobium and tantalum, is still largely unknown. Vanadium in this group is known to give a neutral compound, namely $\text{V}(\text{CO})_6$,² while for niobium and tantalum, the hexacarbonylmetalates only, $[\text{M}(\text{CO})_6]^-$ ($\text{M} = \text{Nb, Ta}$), were reported.³ The synthesis of $\text{V}(\text{CO})_6$ requires the preliminary preparation of $[\text{V}(\text{CO})_6]^-$, which can be carried out by reductive carbonylation at elevated temperature and pressure with magnesium-zinc-diiodine in pyridine⁴ or with sodium metal in diglyme as solvent.³ Similarly, all the known methods to produce $[\text{Nb}(\text{CO})_6]^-$ require the reduction of $\text{Nb}_2\text{Cl}_{10}$ by sodium³ or by the Na-K alloy⁵ in diglyme as

solvent at superatmospheric pressure of CO. While the carbonylation yield of vanadium is around 80%, the reported yields⁵ of $[\text{K}(\text{CH}_3\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OCH}_3)_3][\text{M}(\text{CO})_6]$ ($\text{M} = \text{Nb, Ta}$) are 14%.

This paper reports new and simple procedures for preparing the $[\text{M}(\text{CO})_6]^-$ ($\text{M} = \text{Nb, Ta}$) anions, the former at atmospheric pressure in good yields, and the crystal and molecular structures of both hexacarbonylmetalates as their bis(triphenylphosphine)nitrogen(1+), hereinafter abbreviated as PPN, derivatives, $\text{PPN}[\text{M}(\text{CO})_6]$. Preliminary results of the structure of $\text{PPN}[\text{Nb}(\text{CO})_6]$ have been reported in an earlier publication.⁶ Whenever possible, comparisons among the hexacarbonylmetalate(-I) anions of group 5 elements are made.

Experimental Section

Unless otherwise stated, all of the operations were carried out, with the exclusion of air, under carbon monoxide or argon. Commercially

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Table I. Synthesis of Hexacarbonylmetalates(-I) of Niobium and Tantalum via the Magnesium-Zinc-Pyridine-CO Reductive Carbonylation

run	M, mmol of MCl ₅	cm ³ of pyridine	mmol of I ₂	pCO, ^a atm	t, °C	time, h	mmol of reducing metals ^b				Mg ²⁺ / Zn ²⁺ ^c	CO _{abs} / MCl ₅ ^d	car- bonyl- ation yield, % ^e	[M(CO) ₆] ⁻ yield, % ^f
							Mg	Zn	Mg ²⁺	Zn ²⁺				
1	Nb, 46.6	950	8	1	17	33.0	350	220	198	13	15	7.3	44.5	nd
2	Nb, 67.2	1000	4	1	17	48.0	490	310	377	41	9	6.2	47.1	39.1
3	Nb, 20.1	1000	4	1	17	27.0	148	94	90	6	15	6.6	44.5	29.5
4	Nb, 71.1	1000	0.8	1	17	33.0	503	329	nd	nd		5.6	nd	48.0
5	Nb, 76.1	1000		1	17	48.0	535	362	nd	nd		6.1	46.0	42.4
6	Nb, 2.4	35		1	18	4.3	28		5			2.9	25.0	nd
7	Nb, 3.4	50		1	18	2.4		40		nd		1.7	nd	nd
	Nb, 3.4	50		1	18	4.3		40		4		2.0	28.4	nd
8	Nb, 3.9	50		1	18	4.3	28	18	7	g	v high	3.7	37.0	nd
9	Ta, 13.9	500	2.6	1	17	24.0	110	65	70	3	23	4.0	20.0	6.0
10	Ta, 23.4	350		100	80-85	4.0	126	35	nd	nd		6.2	nd	28.0
11	Ta, 32.8	350		110	80-85	4.0	190	66	nd	nd		8.7	36.0	34.9

^a For experiments carried out at superatmospheric pressure, the initial pressure at room temperature is reported. ^b The cationic species are those present in solution after the carbonylation reaction. ^c Molar ratio. ^d Molar ratio between absorbed CO measured gas volumetrically or manometrically during the reaction and MCl₅ used. ^e Moles of soluble combined CO × 100/moles of MCl₅ × 6. The soluble combined carbon monoxide was determined by decomposition with diiodine-pyridine. ^f Moles of recrystallized [M(CO)₆]⁻ × 100/moles of MCl₅. ^g Trace amounts.

available M₂Cl₁₀ (M = Nb, Ta) were purified by double sublimation at 100–110 °C (ca. 10⁻² mmHg). In the case of particularly impure samples, the chloride was treated with thionyl chloride⁷ at reflux temperature, followed by evaporation of the solvent under reduced pressure and by sublimation of the solid residue. Purification of the pyridine used for the carbonylation reaction was critical and had to be carried out with great care in order to eliminate water completely: after being dried over KOH pellets, it was refluxed over CaH₂ for about 36 h and then distilled, the first portions of distillation being discarded until a persistent violet color of the sodium-naphthalene test was observed. Magnesium and zinc powders were commercially available products used without further purification. The carbon monoxide used was a reagent grade gas that was found to contain variable amounts (1–3%) of molecular hydrogen, but the presence of H₂ was not detrimental to the yields. The magnesium and zinc analyses were carried out with a Perkin-Elmer Model 372 atomic absorption analyzer and by complexometric EDTA titrations. The IR spectra were measured with a Perkin-Elmer Model 283 instrument equipped with grating monochromators, each spectrum being calibrated with both carbon monoxide and water vapor. The IR spectra in aqueous solution were measured in 0.01-mm CaF₂ cells.

Preparation of [Na(THF)[Nb(CO)₆] (Experiment 2 in Table I). The amount (1000 cm³) of pyridine required for the reaction was directly distilled under an atmosphere of prepurified nitrogen into the reaction flask containing a magnetically stirred mixture of magnesium (12 g; 0.49 mol), zinc (20 g; 0.31 mol), and I₂ (1 g; 4 mmol). At the end of the distillation, the flask was evacuated and filled with carbon monoxide, and then freshly sublimed NbCl₅ (18.17 g; 67.2 mmol) was added. The reaction flask was then connected to a gas buret containing carbon monoxide over mercury, and the reaction mixture was vigorously stirred with a magnet. The temperature was maintained at 16 °C by an external water bath operated by a thermostat. Reduction of the chloride occurred promptly, as evidenced by the change of color from yellow-orange to violet and blue. When the color was greenish, a fast carbon monoxide absorption started and continued at the approximate rate of 2 L/h up to a molar CO/Nb ratio of about 3. After that, the rate of the gas absorption decreased. The reaction mixture was stirred for a total about 48 h, when the molar CO/Nb ratio was approximately 6. The red-brown suspension was then decanted for about 12 h and filtered through a medium filter under an atmosphere of carbon monoxide, and the solids on the filter were washed twice with fresh pyridine. The solution showed a strong IR absorption at 1857 cm⁻¹, which is typical of [Nb(CO)₆]⁻ in pyridine solution (vide infra). The quantitative gas analysis (by decomposition with pyridine-I₂ of the coordinated carbon monoxide) on an aliquot of the crude solution showed that the carbonylation yield of soluble carbonyl compounds of niobium was 47%, based on initial niobium. Filtration under carbon monoxide of the crude reaction mixture was

preferred in those experiments planned for the gas volumetric determination of the soluble carbonyl compounds, in order to minimize the experimental errors due to the solubility of carbon monoxide. Filtrations under argon instead of carbon monoxide are not detrimental to the yields of [Nb(CO)₆]⁻. From this point onward, all of the operations were carried out under prepurified argon. The filtered solution was evacuated to dryness (17 °C (ca. 10⁻¹ mmHg)), and the resulting deep brown residue was treated rapidly with 500 cm³ of a 1.2 M aqueous solution of NaOH, while the temperature was controlled by an external ice bath. The resulting orange mixture was extracted several times with diethyl ether free of peroxides (distilled over LiAlH₄ under nitrogen). The combined ether extracts containing sodium hexacarbonylniobate(-I) were evaporated to dryness under reduced pressure, initially with an aspirator and finally with a mechanical pump. The oily yellow-orange residue was treated with 50 cm³ of prepurified tetrahydrofuran, and after the mixture was cooled to dry-ice temperature, the resulting solid was collected by filtration. The hexacarbonylniobate(-I) was then recrystallized by dissolution in tetrahydrofuran (300 cm³) at 40 °C, filtration, and cooling to room temperature. Crystallization was completed by cooling the mother liquor to dry-ice temperature overnight. The sodium derivative was finally separated by filtration and dried in vacuo for about 2 h (9.4 g; 39.1% yield). Anal. Calcd for [Na(C₄H₈O)][Nb(CO)₆], C₁₀H₈NaNbO₇: CO, 47.2; Nb, 26.1. Found: CO, 48.0; Nb, 25.0. The sodium derivative of the [Nb(CO)₆]⁻ anion stabilized by tetrahydrofuran is a yellow-orange solid extremely sensitive to oxygen, obtainable with variable amounts of tetrahydrofuran depending on the residence time in vacuo. Some attempts to obtain a solvent-free compound by prolonged treatment at 20 °C (ca. 5 × 10⁻² mmHg) resulted in complete decomposition to a black, pyrophoric solid. The sodium derivative is quite soluble in diethyl ether, sparingly soluble in tetrahydrofuran at room temperature, and very slightly soluble in dichloromethane, in aromatic hydrocarbons, and in aliphatic hydrocarbons. It is very soluble in water, in which it forms yellow-orange solutions stable under an atmosphere of carbon monoxide, at pH between 7 and 8 or higher. At pH values even slightly lower than 7 (obtained by addition of hydrochloric acid), rapid evolution of carbon monoxide and molecular hydrogen occurred, while with pyridine, HCl, and AcOH/AcO⁻ formation of carbonyl complexes of niobium in higher oxidation states took place.⁸

Preparation of [Na(THF)[Ta(CO)₆]. The carbonylation of Ta₂Cl₁₀ with the Mg-Zn reducing system in pyridine as solvent was shown to occur at atmospheric pressure of carbon monoxide and room temperature with formation of the [Ta(CO)₆]⁻ anion, as indicated by its strong IR absorption at 1852 cm⁻¹. However, the rate of carbonylation was inconveniently slow (see Table I, experiment 9), and the preparation was therefore conducted at higher temperature and pressures. Anhydrous pyridine (run 11 of Table I), prepared

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according to the procedure described above for the preparation of $[\text{Nb}(\text{CO})_6]^-$, was freshly distilled (350 cm³) into a flask containing 11.76 g (32.8 mmol) of freshly sublimed TaCl₅. The resulting orange solution was sucked into a 700-cm³ stainless-steel autoclave containing magnesium (4.63 g; 0.19 mol) and zinc (4.30 g; 0.066 mol) powders. The autoclave was then pressurized with carbon monoxide at 110 atm at room temperature and heated at about 85 °C for 4 h. After the solution was cooled to room temperature (the observed final gas pressure was 90 atm), the gas was vented, the autoclave content was decanted, and the red-brown solution was poured into a 500-cm³ flask under prepurified argon. The solution had an IR absorption at 1852 cm⁻¹, showing that $[\text{Ta}(\text{CO})_6]^-$ was the only predominant carbonyl species present in solution. The gas volumetric analysis (by decomposition with I₂-pyridine) of an aliquot of the decanted solution showed that the yield of carbonylation to soluble carbonyl derivatives was 36% based on tantalum. The pyridine solution of the hexacarbonyltantalate(-I) was evaporated to dryness (16 °C (ca. 5 × 10⁻² mmHg)), and the resulting brown residue was treated rapidly with 350 cm³ of an aqueous 1 M solution of NaOH, while the temperature was kept around 0 °C with an external ice bath. The yellow-orange aqueous alkaline solution was transferred into a separatory funnel and extracted several times with diethyl ether free of peroxides (distilled over LiAlH₄). The combined ether extracts were evaporated to dryness, and the resulting brown oil was treated with 30 cm³ of prepurified tetrahydrofuran to obtain the hexacarbonyltantalate as an orange solid by cooling to dry-ice temperature. The complex was filtered at dry-ice temperature and then recrystallized from tetrahydrofuran by dissolution in 150 cm³ at about 40 °C, filtration, and cooling to room temperature and then to dry-ice temperature. After the complex was filtered and dried in vacuo for 3 h at room temperature, 5.08 g (34.9% yield) of $[\text{Na}(\text{THF})][\text{Ta}(\text{CO})_6]$ was obtained. Anal. Calcd for C₁₀H₈NaO₇Ta: C, 37.8. Found: C, 37.9. The sodium derivative of the $[\text{Ta}(\text{CO})_6]^-$ anion, stabilized by tetrahydrofuran, is an orange solid with stability properties (to both oxygen and heat) and solubility properties similar to those already mentioned above for the corresponding niobium compound.

Attempted Carbonylation of Vanadium. (A) Anhydrous vanadium(III) chloride (7.25 g; 46.0 mmol) was added to a suspension of magnesium (7.0 g; 288 mmol) and zinc (10 g; 153 mmol) in anhydrous pyridine (500 cm³) in an atmosphere of carbon monoxide. The suspension was vigorously stirred for about 48 h under carbon monoxide at atmospheric pressure while the temperature was maintained at 17 °C with a thermostated bath. During this period of time, the solution above the suspended metals became red-brown, but no absorption of carbon monoxide was observed and the IR spectrum of the crude solution did not show any band attributable to a CO stretching vibration.

(B) The above mixture, to which 1 g of I₂ had been added, was stirred under carbon monoxide for an additional 24 h. No gas absorption could be detected, and the IR spectrum of the resulting solution did show the presence of the band at 1851 cm⁻¹, typical of $[\text{V}(\text{CO})_6]^-$, corresponding to about a 2% conversion of the initial vanadium used.

Preparation of the Bis(triphenylphosphine)nitrogen(1+) Derivatives of Niobium and Tantalum, PPN[M(CO)₆]. The niobium derivative was prepared as previously reported⁶ from $[\text{Na}(\text{THF})][\text{Nb}(\text{CO})_6]$ and (PPN)Cl in dichloromethane and recrystallized from dichloromethane-diethyl ether. The preparation of the tantalum compound is reported here in detail, since it is a new compound. The sodium derivative $[\text{Na}(\text{THF})][\text{Ta}(\text{CO})_6]$ (0.182 g; 0.41 mmol) was suspended in dichloromethane (7 cm³) and treated with (PPN)Cl (0.206 g; 0.36 mmol). The reaction was over in a few minutes, as evidenced by the change of color of the precipitate from orange to almost colorless. The solution was filtered, and then diethyl ether (20 cm³) was added to decrease the solubility. Precipitation of the complex was increased by cooling to dry-ice temperature. The complex was filtered and dried in vacuo. Recrystallization was carried out by dissolution in dichloromethane and slow diffusion of diethyl ether (0.225 g; 61.8% yield). Anal. Calcd for $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{N}[\text{Ta}(\text{CO})_6]$, C₄₂H₃₀NO₆P₂Ta: C, 56.8; H, 3.4; N, 1.6. Found: C, 56.5; H, 3.4; N, 1.5.

X-ray Data Collection. Structure Determination and Refinement of PPN[Nb(CO)₆] and PPN[Ta(CO)₆]. The compounds were sufficiently stable to allow the choice of the appropriate crystal to be made in air; the crystals were then sealed in Lindemann capillaries under argon for data collection. Diffraction data were collected on a computer-controlled Siemens AED single-crystal diffractometer by

Table II. Crystal Data and Experimental Details of the X-ray Diffraction Study of PPN[M(CO)₆] (M = Nb, Ta)

	PPN[Nb(CO) ₆]	PPN[Ta(CO) ₆]
molecular formula	C ₄₂ H ₃₀ NNbO ₆ P ₂	C ₄₂ H ₃₀ NO ₆ P ₂ Ta
mol wt	799.56	887.60
cryst syst	rhombohedral	rhombohedral
space group	R $\bar{3}$	R $\bar{3}$
a, Å	9.832 (4)	9.814 (4)
α, deg	91.98 (5)	92.02 (8)
V, Å ³	948.7 (7)	943.4 (7)
Z	1	1
ρ _{calcd} , g cm ⁻³	1.399	1.562
radiation	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
μ, cm ⁻¹	4.32	30.08
F(000)	408	440
scan type	θ-2θ	θ-2θ
2θ range, deg	5-52	5-54
std reflns	2 every 50 data reflcs (244; 126)	1 every 50 data reflcs (114)
total unique data	1068	1302
criterion for observn	I > 2σ(I)	I > 2σ(I)
total obsd data	732	869
no. of parameters varied	100	100
weighting scheme	0.80/σ ² (F _o) + 0.0025F _o ²	0.46/σ ² (F _o) + 0.0022F _o ²
R ^a	0.0391	0.0294
R _w ^b	0.0412	0.0305

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum ||F_o| - |F_c|| / \sum w|F_o|^2]^{1/2}.$$

use of Mo Kα radiation in the θ-2θ scan mode, with the take-off angle set at 4°. Both compounds are rhombohedral, space group R $\bar{3}$. Least-squares refinement of the setting angles of 16 centered reflections led to the unit cell constants reported in Table II in which other relevant crystal data as well as details of the intensity measurements are listed. Standard reflections measured at regular intervals during the course of the experiment showed no significant change in intensity. Data were converted to unscaled F_o values after correction for Lorentz and polarization factors. No absorption or extinction corrections were applied.

The structure of the niobium derivative was determined first, by the conventional heavy-atom method. Isotropic refinement by full-matrix least squares was followed by anisotropic refinement, which converged with a residual R index of 0.0550. At this stage the hydrogen atoms could be located from a difference Fourier map, further refinement (isotropic for hydrogens) yielded the final values listed in Table II. The similarity in cell parameters and intensity data suggested that the niobium and tantalum compounds were isostructural: so, the initial atomic coordinates for the latter structure were assumed from the former, with tantalum replacing niobium. The full-matrix least-squares refinement, with the non-hydrogen atoms refined anisotropically and the hydrogen atoms isotropically, converged to the R values given in Table II. A final difference synthesis showed no residual peak of electron density greater than 0.24 and 0.76 e/Å³ for niobium and tantalum, respectively. No systematic variation of w(F_o - F_c) with F_o or (sin θ)/λ was noted.

Neutral-atom scattering factors and correction for anomalous dispersion effects were obtained from ref 9. Computing with the SHELX-76 system of programs¹⁰ was carried out with the CDC Cyber 76 computer of CINECA (Casalecchio, Bologna). Final atomic positional parameters are listed in Tables III (M = Nb) and IV (M = Ta). Observed and calculated structure factors and thermal parameters are available as supplementary material.

Results and Discussion

Until now, niobium appeared to be the metal of the group 5 triad that had the lowest tendency to undergo reductive

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Table III. Final Fractional Coordinates for PPN[Nb(CO)₆]⁻ (×10⁴ for Nb, P, O, N, C; ×10³ for H)

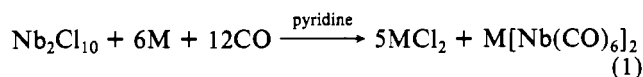
	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Nb	5000	5000	5000
P	939 (1)	939 (1)	939 (1)
O	5948 (4)	2910 (4)	2613 (5)
N	0	0	0
C1	5634 (5)	3651 (5)	3481 (5)
C2	1351 (4)	2490 (3)	127 (3)
C3	2554 (4)	3213 (4)	403 (5)
C4	2780 (6)	4447 (5)	-268 (7)
C5	1847 (7)	4863 (6)	-1193 (6)
C6	655 (6)	4160 (5)	1454 (5)
C7	424 (5)	2973 (4)	-824 (4)
H3	318 (3)	290 (3)	99 (3)
H4	361 (5)	488 (5)	13 (5)
H5	200 (5)	561 (5)	-168 (5)
H6	-2 (6)	455 (6)	-221 (6)
H7	-42 (6)	250 (5)	-102 (5)

Table IV. Final Fractional Coordinates for PPN[Ta(CO)₆]⁻ (×10⁴ for Ta, P, O, N, C; ×10³ for H)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ta	5000	5000	5000
P	940 (1)	940 (1)	940 (1)
O	5941 (5)	2919 (5)	2617 (5)
N	0	0	0
C1	5631 (5)	3656 (6)	3478 (6)
C2	1351 (4)	2497 (4)	114 (4)
C3	2560 (5)	3228 (5)	399 (6)
C4	2793 (5)	4448 (6)	-259 (7)
C5	1846 (7)	4885 (6)	-1185 (7)
C6	658 (6)	4171 (5)	-1469 (5)
C7	415 (5)	2977 (4)	-811 (5)
H3	321 (5)	294 (5)	99 (5)
H4	360 (4)	492 (4)	8 (4)
H5	193 (4)	580 (5)	-166 (5)
H6	-6 (4)	437 (4)	-236 (4)
H7	-40 (5)	244 (4)	-113 (4)

carbonylation. In the original paper,^{3a} [Nb(CO)₆]⁻ was identified by its IR spectrum and no yield was reported. In a subsequent paper,^{3b} a 26.2% yield of the anion was reported, being obtained by superatmospheric pressure carbonylation of Nb₂Cl₁₀ at 105 °C in diglyme as solvent in the presence of iron compounds as promoters and excess sodium metal as reducing agent. As mentioned above, the use of Na-K alloy in diglyme in the presence of Fe(CO)₅ as promoter, at superatmospheric pressure and at ambient temperature, gave moderate yields of the compound in 100 h. The reductive carbonylation of Nb₂Cl₁₀ with sodium metal in diglyme^{3a} in our hands does not occur even at superatmospheric pressure and high temperature.

Our method uses the magnesium/zinc couple as reducing agent and pyridine as "reactive solvent" at atmospheric pressure of carbon monoxide and is carried out at room temperature:



We found that the simultaneous use of both magnesium and zinc powders was beneficial for the carbonylation reaction. Parallel experiments (see runs 6–8 of Table I) carried out with magnesium alone, with zinc alone, and with zinc and magnesium, respectively, showed that the rate of CO absorption and the rate of formation of the soluble [M(CO)₆]⁻ are slower in the first two cases than in the third experiment. Particularly interesting is the case of the experiment with zinc alone, where the CO absorption was somewhat inhibited when the CO/Nb molar ratio was around 1.5. The observed combined effect

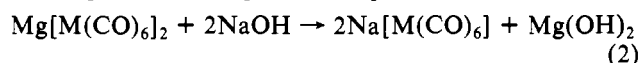
of zinc and magnesium in this reaction is similar to the situation already encountered with the pyridine-Mg/Zn reductive carbonylation of vanadium(III) compounds at superatmospheric pressure of CO and high temperature.¹¹ We believe that the observed synergic effect of the magnesium/zinc couple is due to a preferential adsorption of pyridine at the zinc surface, in agreement with the considerably higher affinity of Zn²⁺ for amines¹² as compared to that of Mg²⁺. Of course, the considerably higher electropositive character of magnesium as compared to that of zinc¹³ will finally induce the electron transfer to occur predominantly at magnesium. As is shown from the data of Table I, we find that magnesium is predominant in solution with respect to zinc, thus showing that the reduction of niobium(V) is largely due to magnesium. In run 8 of Table I, interrupted after a relatively short time, only trace amounts of zinc could be detected in solution.

We believe that pyridine plays an important role in the reductive carbonylation of pentavalent metals. This is presumably due to the formation of the unstable pyridine radical anion in steady-state concentrations during the reaction. The radical anion would then be responsible for the electron-transfer process in a homogeneous phase. It is known¹⁴ that sodium metal and pyridine react to form solutions whose dark blue colors were attributed¹⁵ to the formation of the 4,4'-bipyridyl radical anion. On the other hand, it has already been reported earlier,¹⁶ in connection with the reductive carbonylation of chromium(III) compounds to chromium hexacarbonyl, that magnesium reacts with pyridine to give sparingly soluble blue products, presumably containing the radical anion of pyridine or of its dehydrogenated coupling product.

As may be seen from the data of Table I, a consumption of CO considerably higher than that detectable, as soluble [Nb(CO)₆]⁻ or [Ta(CO)₆]⁻ anions by decomposition with diiodine-pyridine, was constantly observed. The crude reaction mixtures, on the other hand, always showed the carbonyl absorptions of the hexacarbonylmetalates only, thus excluding the presence of significant quantities of other carbonyl complexes in solution. The possibility that sparingly soluble carbonyl compounds of niobium and tantalum can contribute to the CO mass balance is excluded by the observation that no important quantities of combined CO were found in the solid resulting from the filtration of the crude reaction mixture. We therefore conclude that the carbonylation of niobium—and the situation is even more dramatic with tantalum—is accompanied by a parasitic consumption of carbon monoxide to unidentified products.

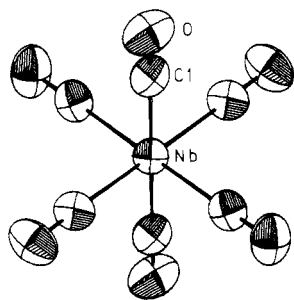
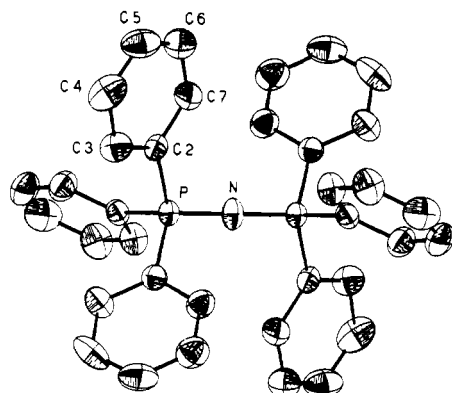
Activation of the reducing metals by diiodine has been used in some of the carbonylation runs but found to be unnecessary, as seen from the data of Table I.

The isolation of [M(CO)₆]⁻ from the crude reaction mixtures requires the aqueous alkaline treatment of the crude solid resulting from the evaporation of pyridine:



The sodium derivatives of the hexacarbonylmetalates of niobium and tantalum are stable in alkaline aqueous solution under an inert atmosphere and are extractable in diethyl ether.

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Figure 1. View of the $[\text{Nb}(\text{CO})_6]^-$ anion.Figure 2. View of the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ cation in $\text{PPN}[\text{Nb}(\text{CO})_6]$.

The reductive carbonylation of tantalum(V) with our system is less effective than that of niobium(V) under comparable conditions. The carbonylation of tantalum(V) occurs also at atmospheric pressure of CO and room temperature (see Table I); however, the rate of reaction was very slow. Considering that VCl_3 under similar mild conditions is carbonylated to a very minor extent, it appears that the Mg-Zn-pyridine-CO system decreases its effectiveness to carbonylate group 5 metals in the sequence $\text{Nb} > \text{Ta} > \text{V}$. The present investigation allows the three sodium salts of the $[\text{M}(\text{CO})_6]^-$ ($\text{M} = \text{V}, \text{Nb}, \text{Ta}$) series to be compared as far as their properties are concerned. The three compounds show a thermal stability that appears qualitatively to decrease in the order $\text{V} > \text{Ta} \approx \text{Nb}$. Cases of decomposition were observed during attempts to eliminate the sodium-coordinated ether solvents from the solids by treatment of the crystalline niobium and tantalum derivatives in vacuo at room temperature. On the contrary, $\text{Na}[\text{V}(\text{CO})_6]$ can easily be obtained solvent free by the same procedure even at temperatures as high as 60°C .¹⁷

The crystal and molecular structures of the bis(triphenylphosphine)nitrogen(1+) derivatives of niobium(-I) and tantalum(-I) have been solved, and both compounds have been found to be isostructural with the corresponding compound of vanadium(-I), i.e. $\text{PPN}[\text{V}(\text{CO})_6]$.¹⁸ Since for both $\text{PPN}[\text{Nb}(\text{CO})_6]$ and $\text{PPN}[\text{Ta}(\text{CO})_6]$ there is only one molecule per unit cell, crystallographic $\bar{3}$ symmetry is imposed on the molecule of the two compounds, with both anions and cations occupying special positions of the space group $R\bar{3}$. In the anion, the metal atom lies on the inversion $\bar{3}$ axis at the special position $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Coordination geometry (Figure 1) is almost exactly octahedral ($\text{Nb}-\text{C} = 2.089(5) \text{ \AA}$, $\text{C}-\text{Nb}-\text{C} = 89.2(2)^\circ$; $\text{Ta}-\text{C} = 2.083(6) \text{ \AA}$, $\text{C}-\text{Ta}-\text{C} = 89.1(2)^\circ$), with the CO groups nearly collinear with the M-C bonds ($\text{Nb}-\text{C}-\text{O} = 177.8(5)^\circ$, $\text{Ta}-\text{C}-\text{O} = 177.9(5)^\circ$). In the cation (Figure 2), the N atom occupies the special position $(0, 0, 0)$ on the $\bar{3}$ axis and coordinates the two triphenylphosphine groups,

Table V. Interatomic Distances (Å) and Bond Angles (deg) of $[\text{Nb}(\text{CO})_6]^-$ and $[\text{Ta}(\text{CO})_6]^-$

	$\text{PPN}[\text{Nb}(\text{CO})_6]$	$\text{PPN}[\text{Ta}(\text{CO})_6]$
M-C1	2.089 (5)	2.083 (6)
C1-O	1.160 (7)	1.149 (8)
C1-M-C1 ^{i a}	89.2 (2)	89.1 (2)
M-C1-O	177.8 (5)	177.9 (5)

^a $i = z, x, y$.

Table VI. Interatomic Distances (Å) and Bond Angles (deg) of $[(\text{PPh}_3)_2\text{N}]^+$ in the Niobium and Tantalum Derivatives

	$\text{PPN}[\text{Nb}(\text{CO})_6]$	$\text{PPN}[\text{Ta}(\text{CO})_6]$
P-N	1.543 (1)	1.541 (2)
P-C2	1.786 (3)	1.795 (4)
C2-C3	1.373 (5)	1.380 (6)
C2-C7	1.390 (6)	1.375 (6)
C3-C4	1.415 (7)	1.396 (8)
C4-C5	1.353 (9)	1.367 (9)
C5-C6	1.352 (9)	1.354 (9)
C6-C7	1.356 (6)	1.375 (7)
N-P-C2	110.7 (2)	110.3 (2)
C2-P-C2 ^{i a}	108.2 (2)	108.6 (2)
P-N-P ^{ii b}	180	180
P-C2-C3	122.2 (3)	121.9 (4)
P-C2-C7	118.7 (3)	118.5 (4)
C3-C2-C7	119.0 (4)	119.6 (4)
C2-C3-C4	118.3 (4)	118.6 (5)
C3-C4-C5	120.1 (5)	120.1 (6)
C4-C5-C6	121.6 (6)	121.5 (6)
C5-C6-C7	119.0 (5)	118.7 (6)
C2-C7-C6	121.9 (5)	121.5 (5)

^a $i = z, x, y$. ^b $ii = \bar{x}, \bar{y}, \bar{z}$.

Table VII. IR Data of Hexacarbonylmetalates of Group 5 Metals in the Carbonyl Stretching Region^a

medium	$\nu_{\text{CO}}, \text{cm}^{-1}$		
	V	Nb	Ta
	$\text{Na}[\text{M}(\text{CO})_6]$		
Et_2O	1923 m	1908 m	1907 m
	1877 vs	1876 vs	1875 vs
	1775 s	1778 s	1777 s
THF ^b	1880 sh	1887 sh	1887 sh
	1851 vs	1860 vs	1857 vs
pyridine	1851 vs	1857 vs	1852 vs
H_2O	1862 vs	1875 vs	1867 vs
	$\text{PPN}[\text{M}(\text{CO})_6]$		
CH_2Cl_2	1852 vs	1854 vs	1852 vs
acetone	1860 vs	1864 vs	1859 vs
THF ^b	1887 sh	1887 sh	1882 sh
	1857 vs	1857 vs	1854 vs
Nujol	1847 vs, br	1850 vs, br	1847 vs, br

^a Spectra in organic solvents were measured in 0.1-mm KBr cells. Spectra in H_2O were measured in 0.01-mm CaF_2 cells. ^b THF = tetrahydrofuran.

whose P atoms lie on the threefold axis. Hence, the PPN moiety is constrained to be centrosymmetric and thus linear at the N atom. In view of the fact that linearity for the cation was also found in the $[\text{V}(\text{CO})_6]^-$ derivative, it is concluded that all three hexacarbonylmetalates of group 5 metals induce linearity in the cation. Whether the linear geometry is the ground-state structure or crystal packing is responsible for the linearity is still a matter of discussion.¹⁹ The phosphorus atoms exhibit a slightly distorted coordination geometry with the C-P-C angles ($\text{M} = \text{Nb}, 108.2(2)^\circ$; $\text{M} = \text{Ta}, 108.6(2)^\circ$)

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(19) For a discussion of the molecular structure of the $[(\text{PPh}_3)_2\text{N}]^+$ cation in several salts, we refer to the paper by Wilson and Bau.¹⁸

significantly smaller than the N–P–C angles ($M = \text{Nb}$, 110.7 (2)°; $M = \text{Ta}$, 110.3 (2)°) (Table VI).

As can be seen from Tables V and VI, there are no significant differences in the corresponding structural parameters of the two compounds. In both structures the anions and the cations are well separated from one another, with no interionic distances being less than 3.35 Å. The shortest contacts O...C(5) (3.396 (8) and 3.382 (9) Å for niobium and tantalum, respectively) are between atoms of molecules related by the inversion center.

The data of Tables V and VI can be compared with the known parameters for niobium²⁰ and tantalum²¹ carbonyl compounds. On the other hand, it has to be considered that no binary carbonyl derivatives of these two metals have been studied crystallographically before and that the lowest oxidation state for which structural data are known is I for both niobium and tantalum. In addition, the data for tantalum carbonyl complexes are very limited in number as yet.²¹

The IR spectra of Table VII are consistent with the octahedral structure of the hexacarbonylmetalates. When the solvent is water or pyridine, only one stretching vibration is in fact observed. In solvents of lower dielectric constant such as tetrahydrofuran and diethyl ether, additional bands are observed that are attributed to distortion of the anion by the counteranion. This effect is well-known²² for other carbo-

nylmetalates. Considering the species of the highest symmetry characterized by the unique carbonyl stretching vibration, it can be concluded that niobium has the highest $\bar{\nu}_{\text{CO}}$ value of the three metals. This is in agreement with what is frequently observed, namely that in families of isostructural compounds the $\bar{\nu}_{\text{CO}}$'s follow the trend $3d < 4d > 5d$.²³ It is interesting to note that the lower degree of π -back-bonding for niobium suggested by the IR data is also in agreement with both the observed higher lability of $[\text{Nb}(\text{CO})_6]^-$, as compared with its analogues, and the tendency, for the cases studied until now,²⁴ of 4d-metal carbonyl derivatives to be kinetically more labile than the 3d and 5d congeners. An intrinsically lower strength or, alternatively, a high polarization of the M–CO bond can be responsible for this behavior. To establish the generality of these observations is a matter of considerable interest, which requires much more work and consideration.

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Registry No. $\text{Na}[\text{V}(\text{CO})_6]$, 15602-41-2; $\text{Na}[\text{Nb}(\text{CO})_6]$, 15602-39-8; $\text{Na}[\text{Ta}(\text{CO})_6]$, 15602-40-1; $\text{PPN}[\text{V}(\text{CO})_6]$, 38856-17-6; $\text{PPN}[\text{Nb}(\text{CO})_6]$, 82738-68-9; $\text{PPN}[\text{Ta}(\text{CO})_6]$, 85454-59-7; NbCl_5 , 10026-12-7; TaCl_5 , 7721-01-9; VCl_3 , 7718-98-1; Mg , 7439-95-4; Zn , 7440-66-6; CO , 630-08-0; pyridine, 110-86-1.

Supplementary Material Available: A figure showing the molecular packing of $\text{PPN}[\text{M}(\text{CO})_6]$ as viewed down the threefold axis and listings of thermal parameters and structure factor amplitudes for $\text{PPM}[\text{Nb}(\text{CO})_6]$ and $\text{PPN}[\text{Ta}(\text{CO})_6]$ (13 pages). Ordering information is given on any current masthead page.

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