

a value of $(6.6 \pm 1.3) \times 10^{-8} \text{ s}^{-1}$.

The rate constant of $2.8 \times 10^{-8} \text{ s}^{-1}$ reported by Wakatsuki lies just within the 3σ error range of our measurement. Agreement may be better than it would appear. Some preliminary observations of ours suggest that the temperature dependence of the rate is significant. Our experiments were conducted at 25 °C, slightly above the temperature of Wakatsuki's experiments. Error estimates were not reported in the earlier work. The error is likely to be of the same magnitude as in our experiments, or larger. The greatest uncertainty in Wakatsuki's number, however, is that it is not clear what was actually measured. No mention was made of the two minor products, 11a-2 and 12a, both of which should have been readily observed. Obviously, the contribution of these products to the kinetics and to the mechanism was not explicitly considered. The description of their experiment simply stated that the reaction was followed by monitoring the intensity change of the cyclopentadienyl resonances.¹⁹ Since the cyclopentadienyl resonances of 2a and 11a-1 disappear and appear at different rates, it is impossible to be certain that the reported rate constant actually pertains to the appearance of 11a-1 rather than the disappearance of 2a. Although we are uncertain, we assume that is was the former of these two possibilities.

Given the difficulties discussed above, we believe that the overall rate constants for the reaction of DPA with 2a determined in the two experiments are in substantial agreement. The third point has now been established. Thus, all available evidence favors the mechanism in Scheme I. 1a is the reactive intermediate in the chemistry of 2a.

Conclusions. This work has demonstrated that the metallacyclic ring of cobaltacyclopentene complexes 2 re-

acts with several unsaturated reagents to afford cyclic organic products. Cobaltaoxanorbornadiene complexes 1, which are in equilibrium with 2, give identical products with these reagents. Coordination of the reagent prior to insertion into the metallacycle ring was demonstrated in two of three cases investigated and was highly probable in the third case. The kinetics of the reaction of 1a with DPA confirmed that 1 is the kinetically significant intermediate in the reactions of 2.

The chemistry of cobaltacyclopentene and cobaltaoxanorbornadiene complexes that we have developed here and in previous papers^{2,3} is specific to complexes with β -carbomethoxy groups. However, no evidence exists that the β -carbomethoxy group plays a role in the mechanism(s) by which ligand-substituted cobaltacyclopentene complexes yield organic products. Thus, insertion reactions of the cobaltacyclopentene ring could be of general utility if a more general route to cobaltacyclopentenes complexes were developed.

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Registry No. 1a, 113158-74-0; 1b, 106800-03-7; 2a, 53559-30-1; 4a, 113087-70-0; 4b, 113087-72-2; 5a, 106800-09-3; 5b, 106800-10-6; 7a, 113087-73-3; 8a, 113087-71-1; 9a, 113087-76-6; 9b, 113087-75-5; 10a, 113087-74-4; 11a⁻¹, 65167-38-6; 11a⁻², 65139-31-3; 13a, 113109-01-6; 14a, 30268-70-3; CpCo(CO)₂, 12078-25-0; CO, 630-08-0; *tert*-butyl isocyanide, 7188-38-7; 2,6-dimethylphenyl isocyanide, 2769-71-3; diphenylacetylene, 501-65-5; 2-carbomethoxy-3,4,5-triphenylcyclopentadienone, 30268-68-9.

Synthesis of Hexacarbonyl Derivatives of Group 5 Metals and Electron-Transfer Processes. Crystal and Molecular Structure of Tetracarbonyl(1,2-bis(diphenylphosphino)ethane)iodotantalum

Fausto Calderazzo,*† Guido Pampaloni,† Giancarlo Pelizzi,‡ and Francesca Vitali‡

Dipartimento di Chimica e Chimica Industriale, Sezione di Chimica Inorganica, Università di Pisa, Via Risorgimento 35, 56100 Pisa, Italy, and Istituto di Chimica Generale and Centro CNR Strutturistica Diffraattometrica, Università di Parma, Viale delle Scienze, 43100 Parma, Italy

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Vanadium, niobium, and tantalum hexacarbonylmetalate(-I) derivatives of several heterocyclic nitrogen bases, $R_nB[M(CO)_6]_n$ ($R = H, Me; n = 1, 2$), have been synthesized. In some cases an electron transfer from the hexacarbonylmetalate to the protonated or methylated BR_n^{n+} cation has been observed. Pyridinium halides react with $Na[M(CO)_6]$ ($M = Nb, Ta$) in the presence of 1 equiv of 1,2-bis(diphenylphosphino)ethane (diphos) to give high yields of the halo tetracarbonyl derivatives $MX(CO)_4(\text{diphos})$. The red-orange $TaI(CO)_4(\text{diphos})$ complex has been studied by X-ray diffraction methods. Crystal data: space group $P2_1/n$; M , 818.3; $a = 14.864$ (10) Å, $b = 9.875$ (7) Å, $c = 19.335$ (13) Å; $\beta = 105.61$ (2)°; $U = 2733$ (3) Å³; $Z = 4$; $D_{\text{calcd}} = 1.988 \text{ g cm}^{-3}$; $F(000) = 1568$; $\mu(\text{Mo K}\alpha) = 52.4 \text{ cm}^{-1}$. The geometry of the seven-coordinate tantalum atom is best described as a capped trigonal prism with the iodide ligand in the capping position. By reaction of $Na[Ta(CO)_6]$ with 1 equiv of hydrogen chloride and diphos in toluene, the hydride $TaH(CO)_4(\text{diphos})$ has been isolated in good yield.

Introduction

Since their discovery in late fifties to early sixties,¹ the binary metal carbonyl derivatives of group 5 metals represent an interesting area of research as far as their syn-

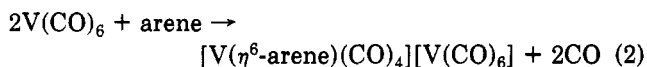
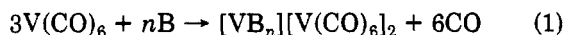
thesis and chemical properties are concerned. For example, the neutral species of vanadium(0), $V(CO)_6$ (no neutral

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*Università di Pisa.

†Università di Parma.

binary carbonyl derivatives of niobium and tantalum are known²), is unique in that it has an odd-valence-electron count and no metal-metal bond is formed. Being a 17-electron species of low-spin d⁵ vanadium(0), it is a long-lived radical that easily undergoes the one-electron reduction to the closed-shell, 18-electron hexacarbonylvanadate(-I) anion, [V(CO)₆]⁻. A typical reaction is the disproportionation in the presence of Lewis bases³ and arenes;⁴ see eq 1 and 2.



The tendency of V(CO)₆ to undergo the one-electron reduction to the [V(CO)₆]⁻ anion is shown by the following examples: (a) the reaction of V(CO)₆ with cycloheptatriene to give both V(η⁶-C₇H₇)(CO)₃ and the disproportionation product [V(C₇H₇)(C₇H₈)] [V(CO)₆]₂⁵; (b) the formation of [V(η⁶-arene)₂][V(CO)₆], [(Me₂N)₂C=C(NMe₂)₂][V(CO)₆]₂ and (η⁵-C₅Me₅)₂V(μ-OC)V(CO)₅ by reaction of V(CO)₆ with V(η⁶-arene)₂,⁶ (Me₂N)₂C=C(NMe₂)₂,⁷ and V(η⁵-C₅Me₅)₂,⁸ respectively; (c) the oxidative carbonylation of VCp₂ (Cp = η⁵-cyclopentadienyl) by V(CO)₆ to give [VCp₂(CO)₂][V(CO)₆].⁹ Moreover, it has recently been shown¹⁰ that V(CO)₆ can also behave as a reducing agent toward bis(cyclopentadienyl) derivatives of Ni(II) and Mn(II), not surprising in view of the zero oxidation state of the metal.

As far as the hexacarbonylmetalates(-I) of vanadium, niobium, and tantalum, [M(CO)₆]⁻, are concerned, it is noteworthy to observe that efficient syntheses of these anions have been developed only recently.¹¹ These anions have interesting redox properties, as shown by the following experimental findings: (a) one-electron transfer from [V(CO)₆]⁻ to protons with formation of dihydrogen and V(CO)₆,¹² (b) two-electron transfer from [M(CO)₆]⁻ (M = Nb, Ta) to a variety of oxidants such as protons, halogens, and salts of Fe(III), Ni(II), Cu(I), Cu(II), Ag(I), and Hg(II) with formation of anionic carbonyl dimers¹³ of formula [M₂(μ-X)₃(CO)₆]⁻; (c) electron transfer from [V(CO)₆]⁻ to organic cations such as tropylium¹⁴ and dithiolium;¹⁵ (d) substitution reactions¹⁶ and formation of

metal-metal bond containing heptacoordinated species.¹⁷

In a recent paper,¹⁸ it has been shown that hexacarbonylvanadate(-I) salts of heterocyclic protonated nitrogen bases can undergo several redox processes such as electron transfer from [V(CO)₆]⁻ to the nitrogen-bonded proton with H₂ evolution or reductive carbon-carbon coupling of the protonated nitrogen base¹⁹ (in the case of acridinium hexacarbonylvanadate(-I), [C₁₃H₁₀N][V(CO)₆]⁻); in both cases, V(CO)₆ is the oxidation product. A study concerning the protonated nitrogen base derivatives of niobium and tantalum hexacarbonylmetalates(-I) was precluded by the easy two-electron transfer from the [M(CO)₆]⁻ anion to the nitrogen-bonded proton of the pyridinium cation with dihydrogen evolution.¹³ On the other hand, the redox chemistry of the [M(CO)₆]⁻ systems was very attractive in view of the possibility to achieve the still unknown Nb(0) and Ta(0) carbonyl derivatives by a one-electron-transfer process.

This paper reports the preparation and properties of the more stable N-methylated heterocyclic base salts of niobium and tantalum hexacarbonylmetalates(-I) and compares their properties with those of the corresponding hexacarbonylvanadates(-I). A high yield method of preparing MX(CO)₄diphos (diphos = 1,2-bis(diphenylphosphino)ethane) is reported, and the X-ray crystal structure of TaI(CO)₄diphos is presented. Moreover, by using diphos as stabilizing ligand, it has been possible to isolate the hydride TaH(CO)₄(diphos) directly from the reaction of Na[Ta(CO)₆] with HCl in hydrocarbon solvents.

Experimental Section

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified nitrogen or argon. Solvents were carefully dried by conventional methods prior to use. IR spectra were measured with a Perkin-Elmer Model 283 instrument equipped with grating. UV-vis spectra were recorded with a Varian Techtron 635 instrument on 10⁻³ M (ε < 3000 M⁻¹ cm⁻¹) or 10⁻⁵ M solutions.

The pyridinium halides, [H-py]X (X = Cl, Br, I), and 1-methylpyridinium iodide, [Me-py]I, were prepared by reacting pyridine with the appropriate halide in *n*-heptane. The colorless solid was filtered, washed with *n*-heptane, and dried in vacuo. [Me-Acr]BPh₄ was prepared by metathesis from [Me-Acr]I with NaBPh₄ in aqueous solution. [Me-Quin]I,²⁰ [Me-Acr]I,²¹ [Me-Nic]I,²² [Me₂bpy(2,2)]I₂,²³ [Me₂bpy(4,4)]I₂,²³ and [Me₂bpy(4,4)]I²⁴

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(19) Abbreviations used for the nitrogen bases (protonation or methylation indicated as H or Me, respectively): pyridine, py; quinoline, Quin; acridine, Acr; 3-pyridinylcarboxamide (nicotinamide), Nic; 2,2'-bipyridine, bpy(2,2'); 4,4'-bipyridine, bpy(4,4'). The sodium and potassium derivatives of the [M(CO)₆]⁻ (M = Nb, Ta) anions have variable amounts of cation-coordinated THF depending on the drying procedure.^{11a,b} The corresponding vanadium derivative can be obtained solvent free.¹²

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Table I. [R-B][M(CO)₆]_n Salts: Analytical Data

R-B ^a	n	M	formula	yield, ^b %	% metal ^c	% CO ^c
H-Nic, 1	1	V	C ₁₂ H ₇ N ₂ O ₇ V	45	15.5 (14.9)	49.1 (49.1)
H ₂ bpy(2,2'), 2	2	V	C ₂₂ H ₁₀ N ₂ O ₁₂ V ₂	77	16.6 (17.1)	55.8 (56.4)
H ₂ bpy(4,4'), 3	2	V	C ₂₂ H ₁₀ N ₂ O ₁₂ V ₂	68	17.0 (17.1)	56.3 (56.4)
Me-Nic, 4	1	V	C ₁₃ H ₉ N ₂ O ₇ V	71	14.4 (14.3)	47.2 (47.2)
Me ₂ bpy(2,2'), 5	2	V	C ₂₄ H ₁₄ N ₂ O ₁₂ V ₂	90	15.8 (16.3)	53.8 (53.8)
Me ₂ bpy(4,4'), 6	2	V	C ₂₄ H ₁₄ N ₂ O ₁₂ V ₂	91	16.1 (16.3)	53.6 (53.8)
Me ₂ bpy(4,4'), 7	1	V	C ₁₈ H ₁₄ N ₂ O ₈ V	96	12.5 (12.7)	41.3 (41.5)
Me-Acr, 8	1	V	C ₂₀ H ₁₂ NO ₆ V	92	12.1 (12.3)	40.4 (40.7)
Me-py, 9	1	Nb	C ₁₂ H ₈ NNbO ₆	91	26.9 (26.2)	47.2 (47.3)
Me-Nic, 10	1	Nb	C ₁₃ H ₉ N ₂ NbO ₇	59	23.0 (23.3)	42.2 (42.2)
Me ₂ bpy(2,2'), 11	2	Nb	C ₂₄ H ₁₄ N ₂ Nb ₂ O ₁₂	81	26.2 (26.2)	47.3 (47.5)
Me ₂ bpy(4,4'), 12	1	Nb	C ₁₈ H ₁₄ N ₂ NbO ₈	89	20.6 (20.8)	37.5 (37.6)
Me-Quin, 13	1	Nb	C ₁₇ H ₁₀ NNbO ₆	81	23.2 (22.3)	40.5 (40.3)
Me-py, 14	1	Ta	C ₁₂ H ₈ NO ₆ Ta	95	41.2 (40.8)	37.8 (37.9)
Me-Nic, 15	1	Ta	C ₁₃ H ₉ N ₂ O ₇ Ta	74	37.0 (37.2)	34.5 (34.6)
Me ₂ bpy(2,2'), 16	2	Ta	C ₂₄ H ₁₄ N ₂ O ₁₂ Ta ₂	97	41.0 (41.0)	37.8 (38.0)
Me ₂ bpy(4,4'), 17	1	Ta	C ₁₈ H ₁₄ N ₂ O ₈ Ta	87	33.3 (33.8)	31.4 (31.4)
Me-Quin, 18	1	Ta	C ₁₇ H ₁₀ NO ₆ Ta	86	35.8 (35.8)	34.0 (33.3)

^aFor the abbreviations used, see ref 19. ^bWith respect to [M(CO)₆]⁻. ^cCalculated analytical values in parentheses.

were prepared according to literature procedures. Sodium hexacarbonylmetalates(-I) of vanadium, niobium, and tantalum, were obtained by methods reported earlier.^{11a,b}

Preparation of Hexacarbonylvanadates(-I) of Protonated Nitrogen Bases, 1-3. Only the preparation of compound 2 is reported in detail, the other compounds being prepared in a similar way. bpy(2,2') (0.17 g, 1.09 mmol) suspended in water (25 mL) was treated with aqueous HCl (2.28 mmol). Na[V(CO)₆] (0.53 g, 2.19 mmol) was then added to the colorless solution which caused the precipitation of [H₂bpy(2,2')][V(CO)₆]₂ as a brown-black solid that was filtered, washed with water (5 × 10 mL), and dried in vacuo over P₄O₁₀; yield 0.50 g (77%). Analytical and spectral data are reported in Tables I and III, respectively.

Preparation of Hexacarbonylmetalates(-I) (M = V, Nb, Ta) of Methylated Nitrogen Bases, 4-18.²⁶ Only the preparation of compound 11 is reported to detail, the other compounds being prepared in a similar way. A solution of [Me₂bpy(2,2')]₂ (0.21 g, 0.48 mmol) in H₂O (25 mL) was treated with Na(THF)_{5,3}[Nb(CO)₆]₁₉ (0.61 g, 0.92 mmol). Immediate precipitation of [Me₂bpy(2,2')][Nb(CO)₆]₂ (11) as a dark brown solid was observed which was collected by filtration and dried in vacuo over P₄O₁₀ (0.27 g, 83% yield). Analytical and spectral data are reported in Tables I and III, respectively.

Reaction of [H₂bpy(2,2')][V(CO)₆]₂ (3) with Sodium Metal. A solution of [H₂bpy(2,2')][V(CO)₆]₂ (3) (0.12 g, 0.2 mmol) in THF (30 mL) was treated with sodium (0.01 g, 0.43 mmol) at room temperature. The brown color of the solution rapidly turned yellow-green with evolution of gas (H₂ by gas chromatography). After 30 h of stirring the solvent was removed in vacuo and H₂O was added to the residue. The yellow solution was filtered and the solid identified as bpy(2,2') from its IR spectrum in Nujol. The solution, after treatment with Bu₄NBr, afforded [Bu₄N][V(CO)₆] (79% yield), identified analytically (CO) and spectroscopically (IR).

Reaction of [Me₂bpy(4,4')][V(CO)₆]₂ (6) with Sodium Metal. A solution of [Me₂bpy(4,4')][V(CO)₆]₂ (6) (0.21 g, 0.34 mmol) in THF (30 mL) was treated with sodium sand (0.008 g, 0.35 mmol) at room temperature. Within few minutes the dark green color changed to violet. After 3 h of stirring at room temperature, the solvent was removed in vacuo and H₂O (20 mL) was added. Analytically (CO) and spectroscopically (IR) pure [Me₂bpy(4,4')][V(CO)₆] (7) (0.12 g, 87%) was separated by filtration and dried in vacuo over P₄O₁₀. By treatment of the filtrate

with Bu₄NBr (0.11 g, 0.34 mmol), 0.13 g (83% yield) of [Bu₄N][V(CO)₆], identified analytically (CO) and spectroscopically (IR), was obtained.

Reaction of [Me₂bpy(4,4')][V(CO)₆] (7) with V(CO)₆. A suspension of [Me₂bpy(4,4')][V(CO)₆] (7) (0.27 g, 0.67 mmol) in toluene (30 mL) was treated with V(CO)₆ (0.153 g, 0.70 mmol). Quickly, the color of the suspension turned green. The mixture was stirred overnight at room temperature and filtered and the solid dried in vacuo affording 0.375 g (86% yield) of analytically (CO) and spectroscopically (IR) pure 6.

[Me-Acr][V(CO)₆] (8). (a) Thermal Decomposition. [Me-Acr][V(CO)₆] (8) (1.0 g, 2.42 mmol) was heated at 40 °C (10⁻² Torr) for 3 h. During this period, the green color of the solid turned gray and a blue-black solid, identified as V(CO)₆ by IR spectroscopy, was collected in a cold trap. The residue (0.44 g, 94%) was identified analytically (C, H, N) and spectroscopically (IR) as 10,10'-dimethyl-9,9'-dihydro-9,9'-biacridyl.²⁶

(b) Attempted Preparation in THF. A suspension of [Me-Acr]BPh₄ (0.83 g, 1.63 mmol) in THF (30 mL) was treated with Na[V(CO)₆] (0.38 g, 1.6 mmol). Evolution of gas and precipitation of a colorless solid were noticed. After 15 h of stirring at room temperature, the solvent was removed in vacuo and the residue treated with water (30 mL) and filtered. The sparingly soluble solid was washed with water, dried, and identified as 10,10'-dimethyl-9,9'-dihydro-9,9'-biacridyl²⁶ (0.3 g, 95% yield) from its IR spectrum in Nujol, ¹H NMR spectrum in CDCl₃, and elemental (C, H, N) analysis. The yellow solution was treated with Bu₄NBr (0.61 g) which caused the separation of [Bu₄N][V(CO)₆] which was filtered and dried in vacuo (0.46 g, 62% yield with respect to Na[V(CO)₆]).

As further confirmation on the stability of 8 in THF, a sample of the compound (0.3 g, 0.73 mmol) prepared in aqueous solution as described above for 11 was treated in the dark with THF (10 mL). Within the time of addition, evolution of gas (CO by gas chromatography) occurred. After 10 h of stirring at room temperature, an IR spectrum of the yellow solution in the carbonyl stretching region revealed the presence of the [V(CO)₆]⁻ anion. After partial evaporation of the solvent, the colorless solid that separated out was filtered and identified as 10,10'-dimethyl-9,9'-dihydro-9,9'-biacridyl from its ¹H NMR spectrum in CDCl₃.

Reaction of [H-Quin]Cl with Na[Nb(CO)₆]. A solution of [H-Quin]Cl (1.44 mmol) in water (30 mL) was treated at room temperature with Na(THF)_{2,3}[Nb(CO)₆] (0.63 g, 1.4 mmol). Evolution of gas (CO and H₂ by gas chromatography) was observed. The resulting red solution was extracted several times with Et₂O, and the collected ether extracts were dried in vacuo. The residue consisted of a mixture of [Nb(CO)₆]⁻ and [Nb₂(μ-Cl)₃(CO)₈]⁻ as shown by an IR spectrum of a THF solution in the carbonyl stretching region. Addition of a second equivalent of [H-Quin]Cl dissolved in water to the extracted mixture caused vigorous evolution of CO and H₂. By operating as described above,

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(25) The nicotinamide derivatives 4, 10, and 15 had the tendency to separate from the aqueous solution as oily products; the latter were washed with dry Et₂O which caused the crystallization of the required product as a brown solid to occur. The compound was filtered and dried in vacuo over P₄O₁₀. The *N*-methylacridinium derivative 8 is sensitive to light and unstable in vacuo with respect to the redox process to V(CO)₆; see Results and Discussion. It was therefore dried over P₄O₁₀ at atmospheric pressure under exclusion of light.

(26) Mader, F.; Zanker, V. *Chem. Ber.* 1964, 97, 2418.

the dimeric anion was found to be the unique carbonyl species.

Similar results were obtained with the hexacarbonyl-tantalate(-I) anion.

Reactions of Na[Nb(CO)₆] with Protons in the Presence of Acridine. (a) **With Dry HCl in THF.** A solution of acridine (0.16 g, 0.89 mmol) and Na(THF)_{2.3}[Nb(CO)₆] (0.29 g, 0.44 mmol) in THF (30 mL) was treated at room temperature with 0.89 mmol of hydrogen chloride, slowly introduced into the reaction mixture with a syringe through a rubber stopper. Evolution of gas was observed (CO by gas chromatography): no H₂ was present in the gas phase. The chloride-bridged dimer [Nb₂(μ-Cl)₃(CO)₈]⁻ was present in solution (IR). Filtration of the solution afforded 9,10,9',10'-tetrahydro-9,9'-biacridyl in 88% yield.

(b) **With CH₃COOH in THF.** A solution of acridine (0.08 g, 0.45 mmol) and K(THF)_{1.8}[Nb(CO)₆] (0.1 g, 0.23 mmol) in THF (30 mL) was stirred for 3 days at room temperature with 0.49 mmol of acetic acid. Gas chromatography of the gas phase showed the presence of CO, no H₂ being present. The IR spectrum of the solution in the carbonyl stretching region had the absorptions due to the [Nb₂(μ-OOCCH₃)₃(CO)₈]⁻ anion¹³ at 2008 m and 1879 vs cm⁻¹. Filtration of the solution afforded 0.06 g (74% yield) of 9,10,9',10'-tetrahydro-9,9'-biacridyl.

(c) **With CH₃COOD in THF.** By operating in the same way as described in (b), 10,10'-dideuterio-9,9'-dihydro-9,9'-biacridyl was obtained in 73% yield. IR (Nujol mull): 3030 w, 2521 w ($\bar{\nu}_{N-D}$), 2501 mw ($\bar{\nu}_{N-D}$), 2481 w ($\bar{\nu}_{N-D}$), 1600 s, 1575 mw, 1355 vs, 1290 s, 1073 mw, 765 m, 755 s, 732 m, 660 m, 435 m cm⁻¹. IR (poly(chlorotrifluoroethylene) mull): 1575 mw, 1472 vs, 1355 vs, 1290 s cm⁻¹.

(d) **With CH₃COOH in THF-d₈.** By operating in the same way as described in (b), 9,10,9',10'-tetrahydro-9,9'-biacridyl was isolated in 70% yield.

Reaction of [Me₂bpy(4,4')]I₂ with Na[M(CO)₆] (M = Nb, Ta). (a) **In H₂O.** A solution of [Me₂bpy(4,4')]I₂ (0.56 g, 1.27 mmol) in H₂O (30 mL) was treated with Na(THF)_{2.3}[Nb(CO)₆] (1.12 g, 2.5 mmol). Evolution of gas (CO by gas chromatography) and precipitation of a violet solid were observed. The solid was filtered, washed with water, dried in vacuo over P₄O₁₀, and identified as [Me₂bpy(4,4')][Nb(CO)₆] (12) (0.55 g) from its analytical data (97% yield with respect to [Me₂bpy(4,4')]I₂); see eq 8. The aqueous solution was extracted several times with Et₂O, and the combined ether extracts were evaporated to dryness under reduced pressure. The IR spectrum of the product in THF solution showed the absorptions due to the [Nb₂(μ-I)₃(CO)₈]⁻ anion.¹³

In the tantalum case, the [Me₂bpy(4,4')][Ta(CO)₆] derivative, 17, was isolated in 96% yield.

(b) **In THF.** In a gas-volumetric apparatus, a suspension of [Me₂bpy(4,4')]I₂ (0.34 g, 0.77 mmol) in THF (25 mL) was treated, under a CO atmosphere, with Na(THF)_{2.3}[Nb(CO)₆] (0.16 g, 0.36 mmol) at 23.6 °C and 762 Torr of total pressure. Evolution of 0.7 mmol of CO (CO/Nb molar ratio of 1.94) was observed within 10 h. The suspension was filtered, and from the filtrate 0.11 g (73% yield) of Na(THF)_{0.3}[Nb₂(μ-I)₃(CO)₈], identified from its IR spectrum (THF) and CO analysis, was collected. The solid, insoluble in THF, was dissolved with water (50 mL); after reduction of the volume under reduced pressure to 10 mL, the solid that precipitated out was filtered and dried over P₄O₁₀ affording 0.16 g (66%) of [Me₂bpy(4,4')]I identified from its UV-vis spectrum in aqueous solution.²⁷

Reaction of [Me-Acr]I Salts with Na[M(CO)₆] (M = Nb, Ta). (a) **In H₂O (M = Nb).** A solution of [Me-Acr]I (0.31 g, 0.48 mmol) in H₂O (30 mL) was treated with Na(THF)_{2.3}[Nb(CO)₆] (0.32 g, 0.48 mmol). Evolution of gas (CO by gas chromatography) and precipitation of a colorless solid was observed. The solid was filtered, washed with water, dried in vacuo over P₄O₁₀, and identified as 10,10'-dimethyl-9,9'-dihydro-9,9'-biacridyl (86% yield). The aqueous solution was extracted several times with Et₂O, and the combined ether extracts were evaporated to dryness under reduced pressure. The IR spectrum of the product (THF) showed the absorptions due to the [Nb₂(μ-I)₃(CO)₈]⁻ anion¹³ and to the [Nb(CO)₆]⁻ anion^{11b} at 2014 m, 1930 w, and 1895 vs cm⁻¹ and 1887 sh, 1860 vs, and 1835 cm⁻¹, respectively.

(b) **In THF (M = Nb, Ta).** In a gas-volumetric apparatus 0.54 mmol of Na(THF)_{2.3}[Nb(CO)₆] in THF (20 mL), treated with 1.07 mmol of [Me-Acr]I at 24.3 °C, gave 1.06 mmol of CO corresponding to a CO/Nb molar ratio of 1.96. When the reaction was repeated on a preparative scale, under the same experimental conditions, 10,10'-dimethyl-9,9'-dihydro-9,9'-biacridyl and Na(THF)_{0.7}[Nb₂(μ-I)₃(CO)₈] were isolated in 80 and 83% yields, respectively. In the case of tantalum, the biacridin derivative was isolated in 84% yield.

Reaction of Na[M(CO)₆] (M = Nb, Ta) with [H-py]X (X = Cl, Br, I) and diphos in THF. Synthesis of MX(CO)₄-(diphos) Derivatives. (a) **X = Cl.** diphos (0.36 g, 0.9 mmol) and [H-py]Cl (0.21 g, 1.8 mmol) suspended in THF (25 mL) were treated at room temperature with Na(THF)_{2.3}[Nb(CO)₆] (0.4 g, 0.89 mmol). Immediate reaction with evolution of CO and H₂ (identified by gas chromatography) was observed. After 2 h of stirring at room temperature the orange-red suspension was filtered, and the filtrate, after partial evaporation of the solvent, was treated with *n*-heptane (30 mL). This operation caused the separation of NbCl(CO)₄(diphos) as an orange-red microcrystalline substance (0.48 g, 84% yield). Anal. Calcd for C₃₀H₂₄ClNbO₄P₂: C, 56.4; H, 3.8. Found: C, 57.0; H, 3.8. By operating under a CO atmosphere, we isolated the tantalum analogue TaCl(CO)₄-(diphos) in 70% yield. Anal. Calcd for C₃₀H₂₄ClO₄P₂Ta: C, 49.6; H, 3.3. Found: C, 50.0; H, 3.42.

A solution of TaCl(CO)₄(diphos) (0.08 g, 0.11 mmol) in toluene (5 mL) was treated under argon with 0.02 mL (0.25 mmol) of dry pyridine. An IR spectrum of the solution in the carbonyl stretching region recorded after 3 h of stirring at room temperature showed absorptions at 2023 s, 1948 m, 1900 vs, and 1883 ms cm⁻¹ due to the starting complex and a new band of medium intensity at 1832 cm⁻¹ (in addition to some shoulders). Upon treatment with carbon monoxide, the new absorption disappeared and the spectrum became identical with the original one. The cycle was repeated three times with similar results. Addition of an excess of pyridine caused evolution of CO and dramatic modifications of the IR spectrum.

(b) **X = Br or I.** A suspension of [H-Py]Br (0.25 g, 1.56 mmol) and diphos (0.32 g, 0.8 mmol) in THF (25 mL) was treated at room temperature under a CO atmosphere with Na(THF)_{2.3}[Nb(CO)₆] (0.33 g, 0.73 mmol). Immediate reaction with evolution of CO and H₂ (identified by gas chromatography) was observed. After 2 h of stirring at room temperature the solvent was removed in vacuo at room temperature and the residue was dissolved in toluene (25 mL) under a CO atmosphere and stirred for 2 h. After filtration, the orange-red solution was treated with *n*-heptane (50 mL) which caused the separation of NbBr(CO)₄(diphos) (0.39 g, 78% yield) as a red-orange microcrystalline solid. Anal. Calcd for C₃₀H₂₄BrNbO₄P₂: C, 52.7; H, 3.5. Found: C, 53.0; H, 3.8. By operating in a similar way, we isolated the following complexes. TaBr(CO)₄diphos: operations carried out under a CO atmosphere; 66% yield. Anal. Calcd for C₃₀H₂₄BrO₄P₂Ta: C, 46.7; H, 3.1. Found: C, 46.8; H, 3.1. NbI(CO)₄(diphos): 76% yield. Anal. Calcd for C₃₀H₂₄NbIO₄P₂: C, 49.3; H, 3.3. Found: C, 49.9; H, 4.0. TaI(CO)₄(diphos): 79% yield. Anal. Calcd for C₃₀H₂₄IO₄P₂Ta: C, 44.0; H, 3.0. Found: C, 44.2; H, 2.9. The IR spectral data are reported in Table V.

Reaction of [M₂(μ-X)₃(CO)₈] Anions (M = Nb; X = Cl, I) with diphos. A solution of Na[Nb₂(μ-I)₃(CO)₈] (0.04 g, 0.04 mmol) in THF (7 mL) was treated with diphos (0.04 g, 0.1 mmol). Immediate reaction took place. An IR spectrum of the red solution in the carbonyl stretching region revealed the presence of NbI(CO)₄(diphos) ($\bar{\nu}_{CO}$ 2024 s, 1959 m, 1909 vs, and 1889 ms cm⁻¹) as the unique carbonyl species.

In a similar way, the [M₂(μ-Cl)₃(CO)₈]⁻ anion was completely converted into NbCl(CO)₄(diphos) ($\bar{\nu}_{CO}$ 2024 s, 1954 m, 1905 vs, and 1885 ms cm⁻¹) by treatment with 2 equiv of diphos.

Reaction of Na [M(CO)₆] with Diiodine in the Presence of diphos. M = V. A suspension of Na[V(CO)₆] (0.59 g, 2.4 mmol) in THF (30 mL) was treated with diiodine (0.62 g, 2.4 mmol) at -78 °C. Evolution of gas and formation of a red solution took place upon mixing of the reagents. When the temperature was about -50 °C, diphos (0.97 g, 2.4 mmol) was added and the mixture was slowly warmed up to -10 °C. The solvent was then removed in vacuo at -10 °C, and the residue was dissolved in toluene (50 mL) and the solution filtered at -10 °C. Addition

(27) Watanabe, T.; Honda, K. *J. Phys. Chem.* 1982, 86, 2617.

of cold *n*-heptane (30 mL) caused the separation of a brown solid that was isolated by filtration and recrystallized from a toluene/*n*-heptane mixture affording 0.39 g (24%) of VI(CO)₄(diphos) as red crystals which decompose in a few hours at room temperature. Anal. Calcd for C₃₀H₂₄IO₄P₂V: C, 52.3; H, 3.5; CO, 16.3. Found: C, 52.9; H, 3.5; CO, 15.8.

M = Nb or Ta. A suspension of Na(THF)_{2.8}[Ta(CO)₆] (0.53 g, 0.9 mmol) in THF (30 mL) was treated with diiodine (0.23 g, 0.9 mmol) at -78 °C. Evolution of gas and formation of a red solution took place upon mixing the reagents. When the temperature was about -50 °C, diphos (0.37 g, 0.9 mmol) was added. After 1 h of stirring at room temperature, the solvent was removed in vacuo, the brown residue dissolved in toluene (25 mL), and the solution filtered obtaining a red solution. By treatment with *n*-heptane (25 mL) and cooling at -30 °C, 0.32 g (42%) of TaI(CO)₄(diphos) were obtained. Anal. Calcd for C₃₀H₂₄IO₄P₂Ta: C, 44.0; H, 3.0. Found: C, 44.1; H, 3.0.

By operating in a similar way, we obtained NbI(CO)₄diphos in 43% yield. Anal. Calcd for C₃₀H₂₄INbO₄P₂: C, 49.3; H, 3.3. Found: C, 49.8; H, 3.3.

TaI(CO)₄(diphos): X-ray Data Collection and Refinement. The crystals for the diffraction experiments were obtained from *n*-heptane-THF (10:1, v/v) at about -30 °C. A crystal of approximate dimensions (mm), 0.28 × 0.42 × 0.58, was sealed in a Lindeman capillary under an argon atmosphere and mounted on a Philips PW 1100 diffractometer with graphite-monochromatized Mo Kα (λ = 0.71069 Å) radiation. The crystal belongs to the monoclinic system with systematic absences (*h*0*l*, *h* + *k* odd, and 0*k*0, *k* odd) characteristic of the centrosymmetric space group *P*2₁/*n*.

Crystal data: space group *P*2₁/*n*; *M*_r, 818.3; *a* = 14.864 (10) Å, *b* = 9.875 (7) Å, *c* = 19.335 (13) Å; β = 105.61 (2)°; *U* = 2733 (3) Å³; *Z* = 4; *D*_{calcd} = 1.988 g cm⁻³; *F*(000) = 1568, μ(Mo Kα) = 52.4 cm⁻¹.

The unit-cell parameters were determined on the basis of a least-squares analysis of the angular settings of 25 strong diffractometer-centered reflections chosen in diverse regions of reciprocal space. Intensities in the range 5.0° < 2θ < 46.0° were measured in the ω-2θ scan type with a scan width of 2.00° and a scan speed of 0.070° s⁻¹. The 2075 unique reflections (±*h*, +*k*, +*l*) obeying the condition *I* > 3σ(*I*) have been retained out of a total of 4187 measured reflections. The reflections were scaled according to the variation of the reference reflection which showed a small change in intensity over the period of data collection. Lorentz, polarization, and absorption corrections were applied, the last correction being empirical and based upon Ψ scans of three reflections near χ = 90° (maximum and minimum transmission factors were estimated to be 1.206 and 1.000, respectively).

The Ta and I atom positions were located via a Patterson map which was calculated by using the complete set of data. After refinement of the positional parameters of these atoms, a subsequent difference Fourier map phased by this model revealed the location of all other non-hydrogen atoms. Atomic coordinates (Table II) were refined by full-matrix least-squares techniques, assuming anisotropic thermal parameters for all non-hydrogen atoms, except for the phenyl rings which were refined isotropically as rigid bodies with fixed hydrogens. The function minimized was Σ*w*|Δ*F*²], where *w* = 1 in the early stages of the refinement and *w* = 2.4424/[σ²(*F*_o) + 0.00065*F*_o²] in the final stages. Refinement converged to *R* = 0.0616 (*R*_w = 0.0756) for 176 variables refined, with the final cycle having all shift-to-error ratios less than 0.1. The largest peak in the final difference Fourier map was 1.5 e Å⁻³ in height and was in vicinity of the tantalum atom.

Complex atom scattering factors were employed, and corrections for both the real and the imaginary components of anomalous dispersion were included for the Ta and I atoms.²⁸ All calculations were performed on a GOULD SEL 32/77 computer using the SHELX 76 suite of programs.²⁹ Other computer programs used have been cited elsewhere.³⁰

Table II. Fractional Atomic Coordinates (×10⁵ for Ta and ×10⁴ for Other Atoms) of TaI(CO)₄(Ph₂PCH₂CH₂PPh₂) with Esd's in Parentheses

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ta	6173 (7)	21927 (10)	38755 (5)
I	1454 (1)	300 (2)	3150 (1)
P(1)	1916 (4)	3777 (6)	3684 (3)
P(2)	15 (4)	3062 (6)	2589 (3)
O(1)	-591 (19)	-358 (23)	3877 (15)
O(2)	-1311 (12)	3194 (18)	3889 (9)
O(3)	761 (11)	3865 (17)	5237 (8)
O(4)	1728 (17)	605 (22)	5217 (12)
C(1)	-217 (22)	593 (30)	3894 (20)
C(2)	-586 (16)	2806 (26)	3886 (14)
C(3)	701 (17)	3298 (25)	4719 (11)
C(4)	1289 (21)	1202 (29)	4731 (14)
C(5)	1601 (14)	4414 (21)	2771 (11)
C(6)	995 (14)	3535 (20)	2230 (10)
C(7)	2250 (9)	5320 (11)	4127 (7)
C(8)	1603 (9)	6096 (11)	4359 (7)
C(9)	1840 (9)	7396 (11)	4630 (7)
C(10)	2724 (9)	7930 (11)	4670 (7)
C(11)	3371 (9)	7142 (11)	4438 (7)
C(12)	3134 (9)	5843 (11)	4167 (7)
C(13)	2978 (8)	2915 (14)	3831 (8)
C(14)	3338 (8)	2400 (14)	4522 (8)
C(15)	4188 (8)	1708 (14)	4697 (8)
C(16)	4677 (8)	1530 (14)	4181 (8)
C(17)	4317 (8)	2045 (14)	3490 (8)
C(18)	3468 (8)	2738 (14)	3315 (8)
C(19)	-656 (10)	1930 (13)	1975 (7)
C(20)	-306 (10)	1280 (13)	1461 (7)
C(21)	-853 (10)	332 (13)	999 (7)
C(22)	-1750 (10)	33 (13)	1050 (7)
C(23)	-2100 (10)	682 (13)	1564 (7)
C(24)	-1553 (10)	1630 (13)	2026 (7)
C(25)	-661 (10)	4561 (11)	2424 (8)
C(26)	-1262 (10)	4853 (11)	1752 (8)
C(27)	-1714 (10)	6103 (11)	1628 (8)
C(28)	-1566 (10)	7061 (11)	2178 (8)
C(29)	-966 (10)	6769 (11)	2850 (8)
C(30)	-513 (10)	5519 (11)	2974 (8)

Reaction of Na[Ta(CO)₆] with Hydrogen Chloride and diphos in THF. Synthesis of TaH(CO)₄(diphos).³¹ A suspension of Na(THF)_{4.9}[Ta(CO)₆] (0.63 g, 0.87 mmol) in toluene (30 mL) was treated at -78 °C with diphos (0.35 g, 0.88 mmol) and slowly added to 0.87 mmol of hydrogen chloride. A change in color of the suspension was noticed even at -78 °C, and, at about -20 °C, vigorous evolution of CO took place (no molecular hydrogen was detected by gas chromatography). The mixture was stirred at room temperature for 24 h and filtered. The red filtrate was treated with *n*-heptane, and the orange microcrystalline solid that separated out was filtered and dried in vacuo, obtaining 0.53 g (77% yield) of TaH(CO)₄(diphos). Anal. Calcd for C₃₀H₂₅O₄P₂Ta: C, 52.0; H, 3.6. Found: C, 52.0; H, 3.6. ¹H NMR (THF-*d*₆, δ values referenced to TMS as internal standard): -3.35 (t, 1 H, *J*_{PH} = 21 Hz), 2.75 (s, 2 H), 3.11 (s, 2 H), 9.0-8.0 (m, 20 H). IR spectrum, see Table V.

Reaction of TaH(CO)₄(diphos) with Dry HCl. A solution of TaH(CO)₄(diphos) (0.12 g, 0.17 mmol) in toluene (5 mL) was treated at -40 °C with 0.17 mmol of dry HCl introduced into the reaction mixture through a rubber stopper. Immediate reaction with evolution gas (H₂ by gas chromatography) took place. The IR spectrum in the carbonyl stretching region of the orange solution showed that TaCl(CO)₄(diphos) (ν_{CO} 2023 s, 1948 m, 1900 vs, 1883 s cm⁻¹) was the only carbonyl species present in solution.

Results and Discussion

Vanadium Complexes. The protonated and/or methylated heterocyclic nitrogen base derivatives, 1-8, of [V(CO)₆]⁻ have been obtained in high yields (Table I) in

(28) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, 1974; Vol. 4.

(29) Sheldrick, G. M. SHELX 76, Program for Crystal Structure Determination, University of Cambridge: Cambridge, England, 1976.

(30) Delledonne, D.; Pelizzi, G.; Pelizzi, C. *Acta Crystallogr., Sect. C: Cryst Struct. Commun.* 1987, C43, 1502.

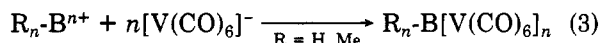
(31) The same compound with comparable properties to ours was recently synthesized by Professor D. Rehder and co-workers, Universität Hamburg (*J. Organomet. Chem.*, in press). We are grateful to Professor Rehder for a copy of the manuscript prior to publication.

Table III. [R-B][M(CO)₆]_n Salts: IR Spectra in the Carbonyl Stretching Region^a

R-B	n	M	ν _{CO} , cm ⁻¹	
			THF	acetone
H-Nic, 1	1	V	1894 w, 1858 vs, 1703 m	1859 vs
H ₂ bpy(2,2'), 2	2	V	1902 m, 1855 vs	1858 vs
H ₂ bpy(4,4'), 3	2	V	1898 mw, 1855 vs	1858 vs
Me-Nic, 4	1	V	1895 w, 1857 vs, 1701 m	1860 vs
Me ₂ bpy(2,2'), 5	2	V	1893 mw, 1858 vs	1860 vs
Me ₂ bpy(4,4'), 6	2	V	b	b
Me ₂ bpy(4,4'), 7	1	V	1893 mw, 1858 vs	1860 vs
Me-Acr, 8	1	V	b	b
Me-py, 9	1	Nb	1890 mw, 1860 vs	1863 vs
Me-Nic, 10	1	Nb	1891 w, 1858 vs, 1706 m	1861 vs
Me ₂ bpy(2,2'), 11	2	Nb	1893 mw, 1860 vs	1859 vs
Me ₂ bpy(4,4'), 12	1	Nb	1890 mw, 1860 vs	1861 vs
Me-Quin, 13	1	Nb	1891 mw, 1861 vs	1863 vs
Me-py, 14	1	Ta	1888 mw, 1859 vs	1859 vs
Me-Nic, 15	1	Ta	1888 w, 1858 vs, 1698 m	1859 vs
Me ₂ bpy(2,2'), 16	2	Ta	1893 m, 1850 vs, 1831 sh	1859 vs
Me ₂ bpy(4,4'), 17	1	Ta	1885 mw, 1858 vs	1859 vs
Me-Quin, 18	1	Ta	1888 mw, 1857 vs	1860 vs

^a0.1-mm CaF₂ cells. ^bDecomposition, see Results and Discussion.

aqueous solution by addition of sodium hexacarbonylvanadate(-I) to an aqueous solution of the appropriate derivative of the protonated or methylated amine, according to eq 3 (*n* = 1 or 2), depending on the nature of B.

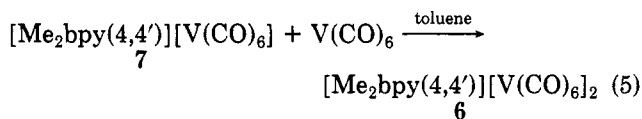
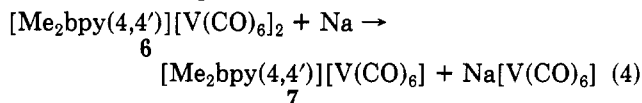


The heterocyclic nitrogen base salts of [V(CO)₆]⁻ are deeply colored (brown to black) both in the solid state and in solvents of low polarity such as Et₂O. This contrasts with the yellow color typical of the [V(CO)₆]⁻ derivatives of alkali tetraalkylammonium and tetraphenylphosphonium cations. Such deep colors are probably due to charge-transfer bands from the [M(CO)₆]⁻ anion to the heterocyclic nitrogen base. Relevant to this point is the X-ray crystal structure of the pyridinium derivative [H-Py][V(CO)₆]⁻,¹⁵ which shows the axial carbonyl groups of the [V(CO)₆]⁻ anion pointing directly to the π-system of the pyridine ring. The color fading (to yellow), observable on going from the solid state to acetone as the solvent, suggests that the cation-anion interactions become weaker with increasing solvent polarity. The IR spectra of the compounds in the carbonyl stretching region (see Table III) show that the solvent with the highest dielectric constant (acetone) causes a rupture of the ion pair [R-B]⁺·[V(CO)₆]⁻, presumably still present in THF solution, with release of the octahedral [V(CO)₆]⁻ anion for which only one IR-active CO stretching vibration is expected. This is a well-established phenomenon for alkali-metal³² cations interacting with carbonylmetalates.

In agreement with the reactivity of hexacarbonylvanadates(-I) of protonated nitrogen bases already reported,¹⁸ compound 2 was found to react with sodium in THF suspension to give Na[V(CO)₆], H₂ evolution, and 2,2'-bipyridine.

The dimethyl-4,4'-bipyridinium derivative, [Me₂bpy(4,4')][V(CO)₆]₂ (6), methylviologen³³ hexacarbonyl-

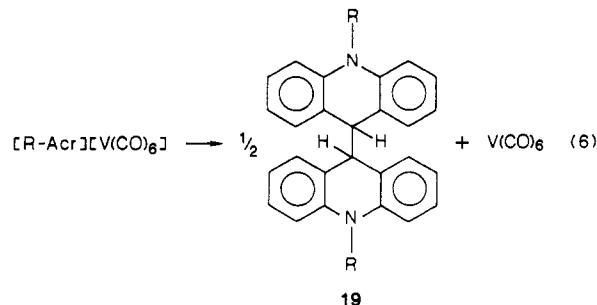
vanadate(-I), can undergo one-electron reduction of the organic cation with formation of compound 7 (eq 4). On the other hand, reoxidation of compound 7 by V(CO)₆ was also observed (eq 5).



This redox behavior of the organic cation is in agreement with the observation that the [Me₂bpy(4,4')]²⁺ cation undergoes reduction to the uncharged species and that the reduction step from the 2+ to the 1+ cation is highly reversible.³³

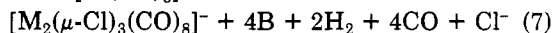
The acridinium derivative deserves some comments. It is known¹⁸ that the reaction of acridinium chloride with Na[V(CO)₆] affords a product of composition [H-Acr][V(CO)₆] which is unstable toward the electron-transfer reaction (eq 5, R = H) both in the solid state or in the presence of a solvent.

The methylated vanadium derivative 8 is similarly unstable, and it cannot be kept for prolonged periods of time even at 0 °C. Its isolation from aqueous solution was successful due to its low solubility which allowed its prompt separation from the other reaction products to be carried out. Attempts to isolate the methyl acridinium derivative in THF solution failed presumably due to the fast interionic electron-transfer reaction (eq 6); this was



established from the high-yield (as high as 90%) isolation of the C-C coupling product (C₁₃H₉NMe)₂ (19, R = Me). The so-formed V(CO)₆ being unstable in THF with respect to the disproportionation reaction,³ [V(CO)₆]⁻ is the metal-containing moiety observed experimentally, to be noted that the photochemical treatment of *N*-methylacridinium halides in ethanol as the solvent^{26,34} yielded 40–20% of the C-C coupled product.

Niobium and Tantalum Complexes. While most of the hexacarbonylvanadate(-I) derivatives of protonated nitrogen bases could be isolated without great difficulties,¹⁸ the attempted isolation of the corresponding niobium and tantalum compounds in water failed due to the two-electron-transfer process M(-I) → M(+I) (M = Nb, Ta). In all cases the dimeric [M₂(μ-X)₃(CO)₈]⁻ anions¹³ were formed according to eq 7. Oxidation to the species of



B = pyridine,¹³ quinoline; M = Nb, Ta

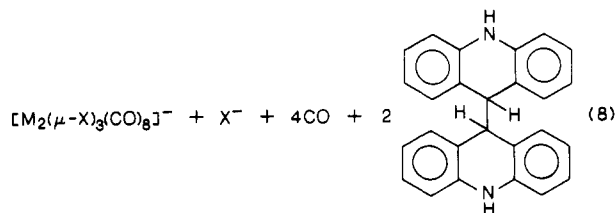
niobium(I) and tantalum(I) occurred also in nonaqueous

(32) (a) Edgell, W. F.; Young, M. T.; Koizumi, N. *J. Am. Chem. Soc.* 1965, 87, 2563. (b) Edgell, W. F.; Lyfor, J. *Ibid.* 1971, 93, 6407. (c) Darensbourg, M. Y.; Borman, C. *Inorg. Chem.* 1976, 15, 3121. (d) Darenbourg, M. Y.; Darenbourg, D. J.; Drew, D. A. *J. Am. Chem. Soc.* 1976, 98, 3127. (e) Edgell, W. F.; Hedge, S.; Barbeta, A. *Ibid.* 1978, 100, 1406. (f) Darenbourg, M. Y.; Hanckel, M. J. *J. Organomet. Chem.* 1981, 217, C9. (g) Calderazzo, F.; Pampaloni, G.; Pelizzi, G. *J. Organomet. Chem.* 1981, 233, C41. (h) Darenbourg, M. Y. *Prog. Inorg. Chem.* 1985, 33, 221.

(33) Farrington, J. A.; Ebert, M.; Land, E. J. *J. Chem. Soc., Faraday Trans.* 1978, 74, 665. Bird, C. L.; Kuhn, A. *Chem. Soc. Rev.* 1981, 10, 49.

(34) Göth, H.; Cerutti, P.; Schmid, H. *Helv. Chim. Acta* 1965, 48, 1395.

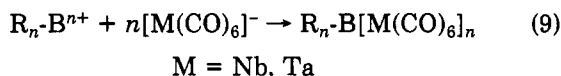
media, such as hydrocarbons and THF. The use of a solvent such as THF was particularly useful with acridine, due to the low solubility of this base in water. In such a case instead of H₂ evolution, reduction of the nitrogen base cation and formation of the C–C coupled product (C₁₃H₉NH)₂ (see eq 8) was observed. This fact is particularly

$$4 \text{Acr} + 2[\text{M}(\text{CO})_6]^- + 4\text{HX} \rightarrow$$


M = Nb, Ta; X = Cl⁻, CH₃COO⁻

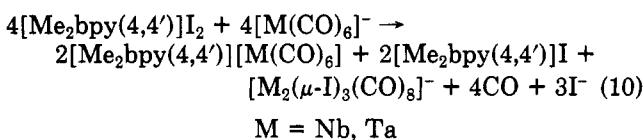
relevant when considering that the same C–C coupled product was obtained even with CH₃COOH as the hydrogen source in THF as solvent. By carrying out the reaction with CH₃COOD, formation of the deuteriated C–C coupled derivative (C₁₃H₉ND)₂ was obtained in good yields; conversely, the use of CH₃COOH in THF-*d*₈ led to the non-deuteriated coupling product (C₁₃H₉NH)₂.

Although the isolation of the protonated niobium and tantalum derivatives was unsuccessful, the corresponding methylated compounds 9–18 were isolated and characterized from aqueous solution, according to eq 9 (*n* = 1, 2).



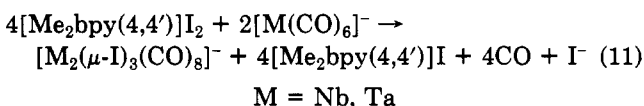
Compounds 9–18 are deeply colored solids soluble in diethyl ether, THF, and acetone. Similar spectroscopic properties to the hexacarbonylvanadate derivatives (see Table III) were observed.

The [Me₂bpy(2,2')]²⁺ and the [Me₂bpy(4,4')]ⁿ⁺ (*n* = 1, 2) systems deserve some comments. An attempted preparation of [Me₂bpy(4,4')][M(CO)₆]₂ (M = Nb, Ta) from aqueous [Me₂bpy(4,4')]I₂ (methylviologen iodide³³) and Na[M(CO)₆] failed due to the reduction of the organic substrate to the radical monocation [Me₂bpy(4,4')]•⁺ and oxidation of the metal to the +I oxidation state, according to eq 10. Due to the low solubility of [Me₂bpy(4,4')][M-



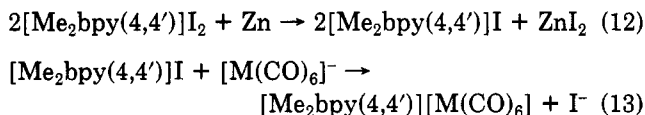
(CO)₆] in the aqueous system used, the radical monocation was recovered in substantially quantitative yields as the hexacarbonylmetalate derivative 12 or 17 (see Table I) in experiments aimed at the isolation of the dication derivative, i.e. carried out in a [M(CO)₆]⁻/[Me₂bpy(4,4')]²⁺ molar ratio of 2/1.

The two-electron oxidation of the hexacarbonylmetalate to the dimeric anionic species [M₂(μ-I)₃(CO)₈]⁻ was demonstrated in experiments carried out in THF, where the correct stoichiometric ratio of the reagents was used; see eq 11.



The hexacarbonylniobate(-I) and tantalate(-I) derivatives of bpy(4,4') could also be obtained in good yields (see

Table I) by first reducing the organic salt [Me₂bpy(4,4')]I₂ with zinc in water²⁴ and then reacting the reduced product with the carbonylate anion (eq 12 and 13). An important

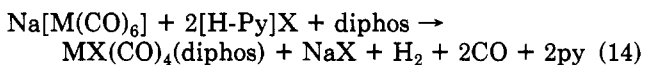


M = Nb, Ta

difference between the [Me₂bpy(2,2')]²⁺ cation and the corresponding "methylviologen" system, [Me₂bpy(4,4')]²⁺, is that no reduction of the former dication was observed. This is in agreement with the higher polarographic half-wave potential of the [Me₂bpy(2,2')]²⁺ cation with respect to [Me₂bpy(4,4')]²⁺.³⁵

Concerning the methylacridinium derivatives of niobium and tantalum, the attempted preparation of [Me-Acr][M(CO)₆] in aqueous solution failed although a transient green color appeared upon mixing of [Me-Acr]I with Na[M(CO)₆] in aqueous solution. Oxidation to the niobium(I) and tantalum(I) species [M₂(μ-I)₃(CO)₈]⁻ was observed instead, with simultaneous reduction of [Me-Acr]⁺ to the C–C coupled product (C₁₃H₉NMe)₂ (19) which was recovered in good yield. The same behavior was observed in nonaqueous solvents, such as THF. The high stability of the niobium(I) and tantalum(I) [M₂(μ-I)₃(CO)₈]⁻ species^{10,13} may explain the failure to prepare the methylacridinium hexacarbonylmetalates, while the corresponding vanadium species, 8, could be isolated in spite of its low stability.

It has already been mentioned that the isolation of protonated nitrogen gas derivatives of niobium(-I) and tantalum(-I) failed due to the fast electron transfer to the proton with dihydrogen evolution and formation of the [M₂(μ-X)₃(CO)₈]⁻ anions; see eq 7. It is reasonable to assume that we are dealing with a carbonyl-mediated electron-transfer process of the type previously suggested for the corresponding vanadium species.¹⁸ The protonated nitrogen base/hexacarbonylmetalate system offered us the possibility of preparing some tetracarbonyl derivatives of tantalum(I), which appeared from earlier studies¹³ on the octacarbonyl anions [M₂(μ-X)₃(CO)₈]⁻ to be much less stable than the corresponding niobium(I) compounds. The bidentate diphos was chosen for this purpose due to its chelating effect and to the well-established stabilizing features in metal-carbonyl chemistry. Under mild conditions, i.e., room temperature or lower, the tetracarbonyl derivatives MX(CO)₄(diphos) were obtained³⁶ according to eq 14. The MX(CO)₄(diphos) derivatives are red-or-



M = Nb, Ta; X = Cl, Br, I

ange crystalline solids slightly sensitive to air in the solid state. The thermal and chemical stability of these compounds appears to decrease in the following sequence: Nb > Ta, I > Br > Cl. In the course of reaction 14, pyridine

(35) (a) Hünig, S.; Gross, J.; Lier, E. F.; Quast, H. *Justus Liebig's Ann. Chem.* 1973, 197, 324. (b) Okura, I.; Kaji, N.; Aono, S.; Kita, T.; Yamada, A. *Inorg. Chem.* 1985, 24, 451.

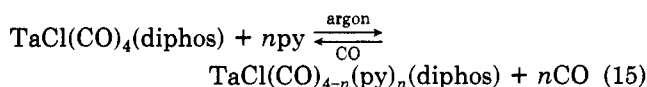
(36) The strictly stoichiometric amount of diphos is to be used in order to avoid the formation of the dicarbonyl derivatives MX(CO)₂(diphos)₂, as evidenced by IR spectral data in comparison with those reported³⁷ for similar complexes with bidentate phosphine ligands MX(CO)₂(PP)₂, obtained by Na-C₁₀H₈ reduction of MX₂(PP)₂ in the presence of CO.

(37) Datta, S.; Wreford, S. S. *Inorg. Chem.* 1977, 16, 1134. Brown, L. D.; Datta, S.; Kouba, J. K.; Smith, L. K.; Wreford, S. S. *Inorg. Chem.* 1978, 17, 729.

Table IV. Selected Bond Distances (Å) and Angles (deg) of TaI(CO)₄(Ph₂PCH₂CH₂PPh₂) with Esd's in Parentheses

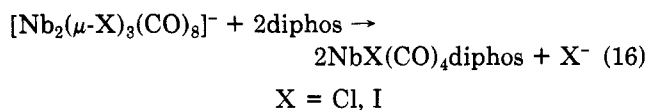
Bond Distances					
Ta-I	2.819 (2)	Ta-C(4)	1.95 (3)	P(2)-C(25)	1.77 (1)
Ta-P(1)	2.588 (6)	P(1)-C(5)	1.81 (2)	C(5)-C(6)	1.47 (3)
Ta-P(2)	2.556 (6)	P(1)-C(7)	1.75 (1)	C(1)-O(1)	1.09 (4)
Ta-C(1)	2.01 (3)	P(1)-C(13)	1.75 (1)	C(2)-O(2)	1.15 (3)
Ta-C(2)	1.89 (3)	P(2)-C(6)	1.83 (2)	C(3)-O(3)	1.13 (3)
Ta-C(3)	1.94 (2)	P(2)-C(19)	1.74 (1)	C(4)-O(4)	1.15 (3)
Bond Angles					
I-Ta-P(1)	83.3 (1)	Ta-P(1)-C(5)	110.0 (7)	P(1)-C(7)-C(8)	120 (1)
I-Ta-P(2)	79.9 (1)	Ta-P(1)-C(7)	125.4 (5)	P(1)-C(7)-C(12)	119 (1)
I-Ta-C(1)	81.1 (9)	Ta-P(1)-C(13)	111.0 (6)	P(1)-C(13)-C(14)	115 (1)
I-Ta-C(2)	139.6 (8)	C(5)-P(1)-C(7)	98.0 (8)	P(1)-C(13)-C(18)	125 (1)
I-Ta-C(3)	148.8 (7)	C(5)-P(1)-C(13)	108.2 (9)	P(2)-C(6)-C(5)	106 (1)
I-Ta-C(4)	84.0 (9)	C(7)-P(1)-C(13)	102.6 (7)	P(2)-C(19)-C(20)	122 (1)
P(1)-Ta-P(2)	74.7 (2)	Ta-P(2)-C(6)	110.3 (7)	P(2)-C(19)-C(24)	118 (1)
P(1)-Ta-C(1)	164.4 (9)	Ta-P(2)-C(19)	115.8 (5)	P(2)-C(25)-C(26)	122 (1)
P(1)-Ta-C(4)	101.1 (9)	Ta-P(2)-C(25)	119.2 (5)	P(2)-C(25)-C(30)	118 (1)
P(2)-Ta-C(1)	103.0 (10)	C(6)-P(2)-C(19)	105.9 (8)	Ta-C(1)-O(1)	171 (3)
P(2)-Ta-C(4)	163.7 (9)	C(6)-P(2)-C(25)	100.9 (8)	Ta-C(2)-O(2)	179 (2)
C(1)-Ta-C(4)	76.6 (13)	C(19)-P(2)-C(25)	102.8 (7)	Ta-C(3)-O(3)	175 (2)
C(2)-Ta-C(3)	70.0 (11)	P(1)-C(5)-C(6)	116 (1)	Ta-C(4)-O(4)	176 (3)

is formed: the possibility of CO substitution by pyridine on the tetracarbonyl product has been established spectroscopically in the case of the least stable metal-halide combination, i.e., TaCl(CO)₄(diphos). With 2 equiv of pyridine, CO substitution was observed, as monitored by IR spectra in the carbonyl stretching region: this reaction was completely reversed under carbon monoxide which suggests the occurrence of the reversible reaction (15). In

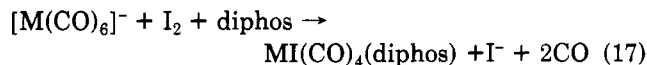


view of the higher lability of the tetracarbonyl complexes containing the lighter halide, the preparation of the chloro and the bromo derivatives had to be carried out under an atmosphere of CO.

The tetracarbonyl derivatives NbX(CO)₄(diphos) are also formed by reacting the dimeric anions [Nb₂(μ-X)₃(CO)₈]⁻ with 2 equiv of diphos (eq 16). Moreover, the iodo



tetracarbonyl complexes of the three metals (V, Nb, Ta) can be prepared by reacting Na[M(CO)₅] with diiodine and diphos in THF at -78 °C (eq 17). By this route it has been



possible to obtain an analytically pure sample of the thermally unstable (it decomposes even at 0 °C under a CO atmosphere) vanadium derivative VI(CO)₄(diphos) previously mentioned³⁸ but incompletely characterized.

In view of the still limited number of crystallographically established complexes of niobium(I) and tantalum(I) not containing cyclopentadienyl ligands,^{10,13,39} it was decided to carry out an X-ray structure determination of TaI(CO)₄(diphos).

An ORTEP drawing of the molecule, also showing the atomic labeling, is shown in Figure 1. Selected bond distances and angles are given in Table IV. The coord-

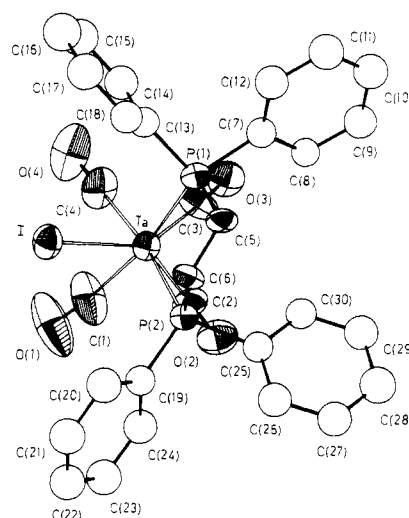


Figure 1. ORTEP view of TaI(CO)₄(Ph₂PCH₂CH₂PPh₂) with the numbering scheme used. Thermal ellipsoids are drawn at the 40% probability level. Anisotropic parameters were used only for shaded atoms.

dination geometry of the tantalum atom is essentially capped trigonal prismatic with the iodide ligand in the capping position, the two phosphorus atoms and two of the carbonyl groups [C(1) and C(4)] in the capped quadrilateral face, and the other two carbonyl groups [C(2) and C(3)] on the remaining edges.

Comparison of the metal-ligand distances with those of similar molecules suffers from a paucity of data: no tantalum(I) derivatives containing iodide ligands have been studied crystallographically. The Ta-I bond distance, 2.819 (2) Å, is comparable to the values of 2.619 (6), 2.704 (4) and 2.932 (7) Å found for (TaI₂)₂,⁴⁰ the only tantalum derivative with such a type of linkage which, to our knowledge, has been characterized by X-ray crystallography. The Ta-P distances of 2.588 (6) and 2.556 (6) Å are in good agreement with those found in two seven-coordinate tantalum complexes containing dmpe as ligand [dmpe = 1,2-bis(dimethylphosphino)ethane], namely 2.567 (1)-2.630 (1) Å in TaCl(η⁴-C₁₀H₈)(dmpe)₂⁴¹ and 2.555(7)-2.623 (7) Å in TaH(PPh₂)₂(dmpe)₂.⁴² The Ta-C

(38) Davison, A.; Ellis, J. E. *J. Organomet. Chem.* **1972**, *36*, 131.

(39) (a) Meakin, P.; Guggenberger, L. J.; Tebbe, F. N.; Jesson, J. P. *Inorg. Chem.* **1974**, *13*, 1025. (b) Leutkens, M. L., Jr.; Santure, D. J.; Huffman, J. C.; Settelberger, A. P. *J. Chem. Soc., Chem. Commun.* **1985**, 552. (c) Leutkens, M. L., Jr.; Huffman, J. C.; Settelberger, A. P. *J. Am. Chem. Soc.* **1985**, *107*, 3361.

(40) Müller, U. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 2502.

(41) Albright, J. O.; Datta, S.; Dezube, B.; Kouba, J. K.; Marynick, D. S.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1979**, *101*, 611.

Table V. IR Spectra of MX(CO)₄(diphos) Derivatives in the Carbonyl Stretching Region^a

M	$\bar{\nu}_{\text{CO}}, \text{cm}^{-1}$	
	THF	toluene
X = Cl		
Nb	2024 s, 1954 m, 1905 vs, 1885 ms	2029 s, 1957 m, 1903 vs, 1885 ms
Ta	2018 s, 1942 m, 1902 vs, 1887 ms	2023 s, 1948 m, 1900 vs, 1883 ms
X = Br		
Nb	2024 s, 1959 m, 1909 vs, 1889 ms	2029 s, 1968 m, 1909 vs, 1884 ms
Ta	2016 s, 1943 m, 1896 vs, 1880 ms	2019 s, 1950 m, 1903 vs, 1880 ms
X = I		
V	2004 s, 1950 m, 1905 vs, 1876 ms	2010 s, 1954 m, 1905 vs, 1874 ms
Nb	2024 s, 1959 m, 1909 vs, 1889 ms	2029 s, 1968 m, 1909 vs, 1884 ms
Ta	2016 s, 1943 m, 1896 vs, 1880 ms	2019 s, 1950 m, 1903 vs, 1880 ms
X = H		
V ^b	1990 m, 1878 vs (br)	
Nb ^c	1998 m, 1875 vs (br)	
Ta	1998 m, 1860 vs (br)	1994 m, 1911 sh, 1892 s, 1863 vs

^a0.1-mm CaF₂ cells. ^bPuttfarcken, U.; Rehder, D. *J. Organomet. Chem.* 1978, 157, 321. ^cBachmann, K.; Rehder, D. *J. Organomet. Chem.* 1984, 276, 177.

distances vary from 1.89 (3) to 2.01 (3) Å with the shorter ones involving the carbonyl groups in the uncapped positions. All are a little shorter than those observed in other carbonyl derivatives of tantalum(I).^{40b,c}

The capping ligand and the atoms at the capped face sites subtend angles of 79.9 (1)–84.0 (9)° at the metal, whereas the atoms at the capped and uncapped face sites subtend angles of 139.6 (8) and 148.8 (7)°. The metal atom deviates 0.31 Å from the plane defined by the four atoms occupying the capped face which are coplanar within 0.004 Å. The Ta–I bond is nearly perpendicular to that plane (86.7°).

The five-membered chelation ring Ta–P(1)–C(5)–C(6)–P(2) shows a C(6) envelope form. The Ta–P–C angles (mean 115.3°) are considerably larger than the C–P–C angles (mean 103.1°), and the P–C_{diphos} distances (mean 1.82 Å) are somewhat longer than the P–C_{Ph} distances (mean 1.75 Å).

As expected, the coordination mode adopted by the carbonyl ligands is essentially linear, the Ta–C–O angles differing from 180° by only 1–9°.

The significant inequivalence of the two nonbonded interactions involving the carbonyl groups at the capped and uncapped face positions [C(1)···C(4) = 2.46 (4) Å and C(2)···C(3) = 2.20 (3) Å] may be qualitatively explained by steric effects associated with the capping ligand.

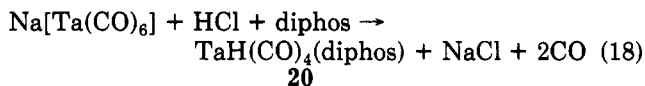
As far as the packing is concerned, it is particularly worth noting that the oxygen atoms of the carbonyls at the capped face positions approach markedly one another through the inversion center [O(1)···O(4) at $\bar{x}, \bar{y}, 1 - z = 2.75$ (4) Å]. Such behavior partly justifies the large thermal motion, which occurs nearly perpendicular to the Ta–C bond, shown by these groups when compared with the other two carbonyls.

The IR spectra (Table V) of the MX(CO)₄(diphos) derivatives in the carbonyl stretching region consist of four

absorptions, in agreement to a virtual C_s symmetry (3A' + A'') of the molecule. To be noted that the $\bar{\nu}_{\text{CO}}$'s of the tetracarbonyl species are almost independent of the nature of the halide ligand. This is unusual since in most of the halo carbonyl complexes there is a trend to a decrease in the wavenumber values in the sequence Cl > Br > I.⁴³ Presumably two compensating effects are operating in this case on the M–CO bond properties such as to cause the observed data.

Earlier papers of this series^{12,18,44} reported that in the reaction of the [V(CO)₆][−] anion with dry HCl in hydrocarbon solvents evidence was obtained for the existence of an unstable hydrogen-containing species formulated as a hydroxycarbyne derivative, (OC)₅VC(OH). The further interaction with amines to give BH⁺[V(CO)₆][−] and the crystal structure of one of the compounds¹⁸ had substantiated this proposal. Niobium and tantalum were predicted to form sufficiently strong M–H bonds, and subsequent work¹³ on the reaction of [Nb(CO)₆][−] and [Ta(CO)₆][−] anions with HX, leading to the two-electron transfer to [Nb₂(μ-X)₃(CO)₈][−], had been rationalized in terms of an unstable hydridic species, HM(CO)₆, reacting with HX to give the cited dimeric anions.

By operating in the presence of a bidentate phosphine, it has now been possible to isolate the hydrido species TaH(CO)₄(diphos) by the reaction of Na[Ta(CO)₆] with dry HCl (eq 18). The compound VH(CO)₄(diphos) had



been synthesized earlier by Davison and Ellis.³⁸ On the basis of the X-ray structural study by Rehder and co-workers⁴⁵ on VH(CO)₄(diphos), the probable solid-state structure of compound 20 may be described as that of a pentagonal bipyramid, with the hydride occupying a position of the pentagonal plane between one CO and one P atom. Moreover, the ¹H NMR spectrum is very similar to those reported for VH(CO)₄(diphos)⁴⁶ and NbH(CO)₄(diphos),⁴⁷ showing a triplet at δ −3.35, thus suggesting that the solution structure of compound 20 is that of a mono-capped octahedron with the hydrido ligand averaged out over the two phosphorus atoms.

The IR spectrum of 20 in toluene as the solvent shows four not well-resolved carbonyl absorptions; in THF only one well-resolved band at 1998 cm^{−1} and a broad asymmetrical band at about 1860 cm^{−1} are present. The existence of species such as C₄H₉OH⁺[Ta(CO)₄(diphos)][−] in solution has to be excluded on the basis of the invariance of the wavenumber values on going from toluene to THF and on the observation that no spectral change was noticed when triethylamine was added to a toluene solution of 20. The failure of TaH(CO)₄(diphos) to behave as a proton donor to the tertiary amine to give [Et₃NH][Ta(CO)₄(diphos)] contrasts with the earlier findings^{18,48} concerning the formation of [H-py]⁺[V(CO)₆][−] and [Et₃NH]⁺[(CO)₃CoCO][−]. On the other hand, VH(CO)₄(diphos) was reported^{46a} to give [Et₃NH][V(CO)₄(diphos)] on treatment with Et₃N. The decrease of the proton acidity on going

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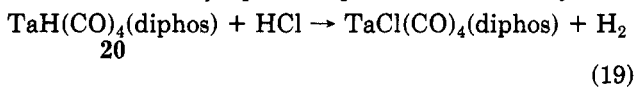
Table VI. [R-B][M(CO)₆]_n Salts: UV-Vis Spectra in THF Solution^a

R-B	n	M	wavelength, ^b nm
H-Nic, 1	1	V	355 (8040)
H ₂ bpy(2,2'), 2	2	V	382 (7320)
H ₂ bpy(4,4'), 3	2	V	357 (8730), 585 (418)
Me-Nic, 4	1	V	358 (6190)
Me ₂ bpy(2,2'), 5	2	V	381 (5934)
Me ₂ bpy(4,4'), 6	2	V	c, d
Me ₂ bpy(4,4'), 7	1	V	372 (16500), 388 (24000), 399 (35640), 610 (12100), 739 (2860)
Me-Quin ^{e,f}	1	V	320 (10410), 350 (6830), 635 (140)
Me-Acr, 8	1	V	c
Me-py, 9	1	Nb	382 (12940)
Me-Nic, 10	1	Nb	356 (6540)
Me ₂ bpy(2,2'), 11	2	Nb	380 (6063)
Me ₂ bpy(4,4'), ^f	1	Nb	372 (18970), 388 (27140), 399 (39530), 610 (11980), 740 (2670)
Me-Quin, ^{e,f} 13	1	Nb	320 (10360), 350 (6350), 650 (220)
Me-py, 14	1	Ta	382 (12940)
Me-Nic, 15	1	Ta	357 (5840)
Me ₂ bpy(2,2'), 16	2	Ta	380 (5960)
Me ₂ bpy(4,4'), ^g 17	1	Ta	372 (18000), 388 (25880), 399 (37900), 610 (11500), 739 (2320)
Me-Quin, ^{e,f} 18	1	Ta	320 (10500), 350 (6750), 620 (290)

^a Only the fully resolved absorptions are reported. ^b Molar extinction coefficients (M⁻¹ cm⁻¹) in parentheses. ^c Decomposition, see Results and Discussion. ^d UV-vis spectrum in acetonitrile: 350 nm (6960 M⁻¹ cm⁻¹). ^e Reported in ref 18. ^f UV-vis spectrum of [Me-Quin]I in water: 320 nm (10470) M⁻¹ cm⁻¹. ^g UV-vis spectrum in acetone solution: 387 (32720), 397 (42700), 609 (12740), 735 nm (2370 M⁻¹ cm⁻¹).

from a 3d to a 5d species is in agreement with what was observed in other systems containing a metal-hydrogen bond⁴⁹ and may be related to a correspondingly stronger M-H bond.

Nevertheless, the hydridic nature of TaH(CO)₄(diphos) is strongly evidenced by the reaction with dry HCl in toluene yielding molecular hydrogen and the chloro derivative TaCl(CO)₄(diphos) (eq 19). The tendency of 20



to give the chloro derivative is so strong that in the course of reaction 19, slow addition of HCl is required in order to optimize the formation of the hydride.

Electronic Spectra. The UV-vis spectra of the compounds in THF solution are reported in Table VI. Three sets of absorptions are observed, namely: (a) an absorption band in the range 350–400 nm due to the [M(CO)₆]⁻ anion (assigned⁵⁰ to a M → π*_{CO} charge-transfer band); (b) for compounds 7, 12, 17, 13, 18, and [Me-Quin][V(CO)₆], bands at 388, 399, 610, 740, and 320 nm, respectively, persistent in acetone solution and present in the halide derivatives of the same counterion, attributed to an absorption of the organic moiety; (c) for compounds 3, 13, 18, and [Me-

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Quin][V(CO)₆] bands at 585, 650, 620, and 635 nm, respectively, with molar extinction coefficients ranging from 140 to 420 M⁻¹ cm⁻¹, which are attributed to the charge-transfer band within the ion pair. It is noteworthy to observe that neither the cation nor the anion have absorptions of comparable intensity in this region of the spectrum. These bands disappear in acetone solution, due to the separation of the ion pair by the solvent, in agreement with the differences encountered in the IR spectra (see Table II) on going from THF to acetone solutions. Similar charge-transfer bands with molar extinction coefficients around 50 M⁻¹ cm⁻¹ were measured for the [Me₂bpy(4,4')]²⁺...[Fe(CN)₆]⁴⁻ ion pair.⁵¹ Compound 6 appears to be stable in the solid state only. In THF a rapid change of color of the solution from yellow-green to dark blue has been observed: the UV-vis spectrum of the solution revealed the presence of the radical cation MV^{•+}.²⁷ Independent gas-volumetric measurements showed that CO was evolved up to a CO/V molar ratio of 1.08 after ca. 48 h. These observations can be rationalized by taking into consideration the two competitive reactions described in eq 1 and 5. A similar behavior was observed in solvents with dielectric constants similar to that of THF (ε = 7.58⁵²), such as methyl and ethyl acetate (ε = 8.02 and 6.00, respectively⁵²). However, in acetonitrile (ε = 37.5⁵²), the electron-transfer reaction appears to be substantially suppressed as shown by UV-vis spectroscopy in the 300–900 nm region, due to the ion-pair separation by the solvent.

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Registry No. 1, 112713-37-8; 2, 112739-79-4; 3, 112713-38-9; 4, 112713-39-0; 5, 112713-40-3; 6, 112713-41-4; 7, 112713-43-6; 8, 112713-44-7; 9, 112713-45-8; 10, 112713-46-9; 11, 112713-47-0; 12, 112713-49-2; 13, 112713-50-5; 14, 112713-51-6; 15, 112713-52-7; 16, 112713-53-8; 17, 112713-55-0; 18, 112713-56-1; 19 (R = Me), 3295-69-0; 19 (R = H), 4838-42-0; 19 (R = D), 112713-63-0; Nic, 98-92-0; bpy(2,2'), 366-18-7; bpy(4,4'), 553-26-4; [Me-Nic]I, 1005-24-9; [Me₂bpy(2,2')]I₂, 31722-01-7; [Me₂bpy(4,4')]I₂, 1910-42-5; [Me-Acr]I, 5776-39-6; [Me-py]I, 7680-73-1; [Me-Quin]I, 2525-21-5; [H-py]Cl, 628-13-7; [H-py]Br, 18820-82-1; Acr, 260-94-6; diphos, 1663-45-2; [Me-Acr]BPh₄, 29013-57-8; [H-Quin]Cl, 530-64-3; [Nb₂(μ-Cl)₃(CO)₄]⁻, 84821-60-3; K[Nb(CO)₆], 57574-57-9; NbCl(CO)₄(diphos), 112713-62-9; TaCl(CO)₄(diphos), 112713-61-8; NbBr(CO)₄(diphos), 112713-60-7; TaBr(CO)₄(diphos), 112713-59-4; TaI(CO)₄(diphos), 112713-58-3; Na[Nb₂(μ-I)₃(CO)₆], 102858-32-2; VI(CO)₄(diphos), 36643-83-1; NbI(CO)₄(diphos), 112713-57-2; TaH(CO)₄(diphos), 111532-98-0; Na[V(CO)₆], 15602-41-2; Na[Nb(CO)₆], 15602-39-8; Na[Ta(CO)₆], 15602-40-1; [Bu₄N][V(CO)₆], 56328-27-9.

Supplementary Material Available: Tables of crystal data, anisotropic thermal parameters, fractional atomic coordinates for hydrogen atoms, and complete bond lengths and angles (6 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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