Table I. Observed and Calculated Vertical Ionization Potentials of Biferrocenylene (**1**) and Biferrocene (**2**) (All Values in eV)

peak	$I_{V,J}$	assignt		MO type/dominant contribn[b]	$(-\epsilon_J)I_{V,J}^K$	$I_{V,J}^{\Delta SCF}$		$I_{V,J}^{TOM}$	
		MO	no.			deloc	loc	deloc	loc
				Biferrocenylene					
1	6.55_{sh}	$8b_{3u}$	51	$d_{z^2} - d'_{z^2}$	10.97	9.43	7.83	8.71	6.10
		$9a_g$	49	$d_{z^2} + d'_{z^2}$	11.14	9.47	7.83	8.96	6.10
		$5b_{1g}$	46	$d_{xy} + d'_{xy}$	11.34	9.97	8.29	9.25	6.92
	7.0_{max}	$7b_{3u}$	45	$d_{x^2-y^2} - d'_{x^2-y^2}$	11.42	9.40	8.12	8.48	6.70
	7.1_{max}	$5b_{2u}$	44	$d_{xy} - d'_{xy}$	11.48	9.91	8.29	9.21	6.92
		$8a_g$	42	$d_{x^2-y^2} + d'_{x^2-y^2}$	11.63	9.80	8.12	8.12	6.70
2	7.85	$9b_{3u}$	56	F_π	8.88	8.51	*a*	8.30	*a*
3	8.8_{max}	$6b_{1g}$	55	F_π	10.05	9.74		9.74	
		$6b_{2u}$	54	F_π	10.25	9.94		9.94	
		$10a_g$	52	F_π/Fe $3d_{z^2}$	10.79	9.99		9.28	
		$7b_{2g}$	53	F_π/Fe d_{xz}	10.63	10.09		9.92	
	9.1_{max}	$5a_u$	50	F_π/Fe d_{yz}	11.09	10.84		10.69	
		$5b_{3g}$	48	F_π/Fe d_{yz}	11.22	10.91		10.78	
		$8b_{1u}$	47	F_π/Fe d_{xz}	11.33	11.18		11.02	
	9.9_{max}	$6b_{2g}$	43	F_π	11.61	11.41		11.37	
				Biferrocene					
1	6.6_{sh}	$17a_g$	53	$d_{z^2} + d'_{z^2}$	10.76	9.24	7.68	8.46	6.16
		$16b_u$	52	$d_{z^2} - d'_{z^2}$	10.84	9.44	7.68	8.58	6.16
		$15b_u$	48	$d_{x^2-y^2} - d'_{x^2-y^2}$	11.30	9.81	8.33	8.90	6.94
	6.8	$9a_g$	47	$d_{xy} + d'_{xy}$	11.32	9.80	*a*	9.09	*a*
	7.1	$15a_g$	46	$d_{x^2-y^2} + d'_{x^2-y^2}$	11.33	9.49	8.33	8.91	6.94
		$9a_u$	45	$d_{xy} - d'_{xy}$	11.36	9.80	*a*	9.08	*a*
2	8.0	$18a_g$	57	F_π	9.36	8.87		8.71	
3		$11a_u$	56	F_π/Cp_π	10.09	9.74		9.80	
	8.8_{max}	$11b_g$	55	F_π/Cp_π	10.21	9.91		9.94	
		$17b_u$	54	Cp_π	10.47	10.18		10.14	
		$16a_g$	51	Cp_π/Fe $3d_{xz}$	11.05	10.68		10.44	
	9.2_{max}	$10b_g$	50	$F_\pi/Cp_\pi/3d_{yz}$	11.17	10.82		10.65	
		$10a_u$	49	$F_\pi/Cp_\pi/3d_{yz}$	11.21	10.84		10.73	
	9.8_{sh}	$14b_u$	44	$F_\pi/3d_{x^2-y^2}/3d_{xz}$	11.50	10.64		10.36	

[a] The ΔSCF and TOM procedures did not converge into localized hole states within the $3d_{xy}$ pair. [b] F ≡ fulvalenyl ligand; Cp ≡ cyclopentadienyl ligand.

remaining peaks below 11 eV in both spectra correspond to ionization events from orbitals with dominant ligand character. The second band in both spectra arises from the ionization of the highest occupied orbital (HOMO) of **1** and **2**, $9b_{3u}$ and $18a_g$, respectively. This orbital is closely related to the b_{2g} (HOMO) of fulvalene and is absent in ferrocene. A comparison of the intensity of band 3 with that of band 2 suggests[18] that there are eight ionization processes in **1** and seven in **2**. The first two maxima of band 3 in the case of **1** are assigned as due to the ionization out of $6b_{1g}$, $6b_{2u}$, $5a_u$, and $5b_{3g}$. These linear combinations are related to the ferrocene e_{1u} and e_{1g} orbitals. In **2** band 3 is not resolved. Our calculation predicts that relaxation effects for the latter ionization events are only of minor importance.

Our model calculations on the ground state of **1** and **2** suggest that the highest occupied molecular orbitals of **1** and **2** are levels with dominant ligand character. The most stable cation, however, is generated by removing an electron from a 3d level, due to the large rearrangement effects discussed before. This result, which is consistent with our PE measurements, contradicts a recent study on $\mathbf{2}^+$. On the basis of a Mössbauer spectroscopic investigation on $\mathbf{2}^+$, it was concluded[19] that the unpaired electron of $\mathbf{2}^+$ is predominantly housed in a ligand orbital.

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Registry No. **1**, 11105-90-1; **2**, 1287-38-3.

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(15) The hole-state nature of $\mathbf{1}^+$ and $\mathbf{2}^+$ is due to the fact that metal–metal interaction is small as a result of the large separation between the two Fe centers (3.90 Å in **1**,[16] 5.08 Å in **2**[17]). The larger Fe–Fe distance in **2** compared with that in **1** reduces the energy gap between the Fe 3d g/u pairs by a factor of 2–3. Consequently a faster hole exchange between the two iron sites in **1** compared with that in **2** is to be expected.

(16) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **8**, 1970 (1969).

(17) Z. L. Kaluski, J. T. Struckow, and R. L. Avoyan, *Z. Strukt. Khim.*, **5**, 743 (1964); A. C. McDonald and J. Trotter, *Acta Crystallogr.*, **17**, 872 (1964).

(18) The areas below the envelopes of band 3 and band 2 yield the following ratios: **1**, 7.8:1; **2**, 6.6:1.

(19) A. W. Rudie, A. Davison, and R. B. Frankel, *J. Am. Chem. Soc.*, **101**, 1629 (1979).

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Synthesis and Properties of (Triphenylphosphine)pentacarbonylvanadium(0), $V(CO)_5Ph_3P$

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Reactions of hexacarbonylvanadium with triphenylphosphine are known to be very solvent dependent.[1] Thus, $V(CO)_6$ and triphenylphosphine in diethyl ether yield the disproportionation product[2] shown in eq 1, while the same

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(1) For a review on $V(CO)_6$ chemistry see J. E. Ellis, *J. Organomet. Chem.*, **86**, 1 (1975).

(2) W. Hieber, J. Peterhans, and E. Winter, *Chem. Ber.*, **94**, 2572 (1961).

0020-1669/80/1319-1082$01.00/0

reactants in hexane have been previously reported to yield only bis-substituted vanadium carbonyl (eq 2).[2,3] Since $V(CO)_6$

$$3V(CO)_6 + 2Ph_3P + 6Et_2O \rightarrow [V(Et_2O)_6][V(CO)_5Ph_3P]_2 + 8CO \quad (1)$$

$$V(CO)_6 + 2Ph_3P \xrightarrow{\text{hexane}} V(CO)_4(Ph_3P)_2 + 2CO \quad (2)$$

rapidly disproportionates in ether and in other donor solvents (B) to yield salts of composition $[VB_n][V(CO)_6]_2$ (eq 3)[2,4] it

$$3V(CO)_6 + nB \rightarrow [VB_n][V(CO)_6]_2 + 6CO \quad (3)$$

$$B = \text{various donor solvents}$$

has been suggested that $V(CO)_5PPh_3^-$, formed by addition of PPh_3 to solutions of $V(CO)_6$ in ether, arises by substitution of $V(CO)_6^-$ after disproportionation.[5] Yet other workers have shown $V(CO)_6^-$ to be inert to thermal substitution of triphenylphosphine under a variety of conditions (e.g., in molten triphenylphosphine).[6] On this basis it seemed more likely that the formation of $V(CO)_5Ph_3P^-$ occurs via initial formation of a substituted neutral vanadium carbonyl species in ether which then disproportionates to the observed salt.[7] To test this hypothesis, we reinvestigated the $V(CO)_6$–PPh_3 reaction. Under a variety of conditions this reaction provided only $V(CO)_5Ph_3P$, the first example of a neutral monosubstituted pnicogen derivative of $V(CO)_6$. In this paper preparations and properties of this new material will be presented and discussed with respect to previous observations on this system. Also described are improved preparations of $[Et_4N][V(CO)_6]$ and $V(CO)_6$.

Experimental Section

General Procedures and Materials. All operations were carried out under an atmosphere of purified nitrogen further purified by passage through columns of activated BASF catalyst, anhydrous magnesium perchlorate, and 13× molecular sieves. Solutions were transferred by stainless-steel cannulae and syringes; otherwise reactions were performed by using standard Schlenk apparatus.

Reagent grade diethyl ether and tetrahydrofuran (THF) were freshly distilled from the benzophenone ketyl of potassium under a nitrogen atmosphere. Methylene chloride, toluene, isopentane, acetone, and methanol were obtained from commercial sources and purged with nitrogen to remove air before use. Triphenylphosphine was recrystallized from hot ethanol under nitrogen to remove triphenylphosphine oxide. Bis(diglyme)sodium hexacarbonylvanadate was purchased and converted to the tetraethylammonium salt as shown below. All other reagents were obtained from commercial sources and freed of oxygen before use. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer by using sealed sodium chloride solution cells. Analyses were performed by Malissa and Reuter Analytische Laboratorien and Spang Microanalytical Laboratory. Professor Louis Pignolet kindly determined the magnetic moment of $V(CO)_5PPh_3$ by the Faraday method.

Preparation of $[Et_4N][V(CO)_6]$. A rather difficult procedure for the synthesis of this salt from unsolvated $Na[V(CO)_6]$ and $[Et_4N]Cl$ in liquid ammonia at −40 °C has been reported.[6b] Here we report a facile, high-yield preparation from commercially available $[Na(diglyme)_2][V(CO)_6]$ and from less costly $[Et_4N]Br$.

In a typical metathesis, 32 g of $[Na(diglyme)_2][V(CO)_6]$ is dissolved in oxygen-free acteone (50 mL) and is added with stirring to an oxygen-free aqueous solution of $[Et_4N]Br$ (40 g, 3 equiv, in 100 mL of water). Immediate precipitation of yellow product occurs. Acetone is removed from solution in vacuo to ensure complete recovery of product. The solid is filtered (medium-porosity fritted disk), washed thoroughly with water (2 × 20 mL), and dried in vacuo. Analytically pure yellow, powdery $[Et_4N][V(CO)_6]$ was obtained in 90% yield (ca. 20 g). However, yields do vary, according to how much free diglyme is present in the commercial bis(diglyme)sodium salt. Anal. Calcd for $C_{14}H_{20}NO_6V$: C, 48.15; H, 5.77. Found: C, 48.26; H, 5.83 (decomposes before melting above 173 °C). Dry $[Et_4N][V(CO)_6]$ is stable in dry air for many hours; however, the moist salt reacts slowly with air to provide an impure yellow-green product.

Preparation of $V(CO)_6$. $V(CO)_6$ was prepared by a modified method of Silvestri et al.[8] by reacting $[Et_4N][V(CO)_6]$ with crystalline 100% orthophosphoric acid (MCB Chemical, Inc.) at 40–50 °C. Typically, a 250-mL flask equipped with a water-cooled sublimation probe is charged with 4 g of $[Et_4N][V(CO)_6]$ and 30 g of 100% H_3PO_4. Initially, the flask is evacuated to ca. 0.1 mmHg and then isolated from the vacuum pump. Slow stirring is commenced while the reaction mixture is heated to 40–45 °C (slow stirring is essential to minimize contamination of the $V(CO)_6$ on the probe with H_3PO_4 and/or $[Et_4N][V(CO)_6]$). After ca. 12 h of sublimation, 2.0 g (80% yield) of lustrous bluish black $V(CO)_6$ crystals was obtained. Higher yields may be obtained by using a dry ice–actone-cooled sublimation probe. Although crystalline $V(CO)_6$ is generally not pyrophoric, it must be removed from the probe in a drybag or drybox.

Preparation of $V(CO)_5Ph_3P$. a. From $V(CO)_6$ and Ph_3P. Hexacarbonylvanadium (0.50 g, 2.28 mmol) was dissolved in 20 mL of cold (CH_2Cl_2 (−70 °C)). One equivalent of triphenylphosphine (0.60 g, 2.28 mmol) in 20 mL of CH_2Cl_2 was cooled to −70 °C and added dropwise to the $V(CO)_6$ solution with stirring. After all PPh_3 was added, the resulting clear yellow-orange solution was stirred at 0 °C for 1.5 h. Infrared monitoring of reaction showed all $V(CO)_6$ to be absent. Hexane (20 mL) was added, and most CH_2Cl_2 was removed in vacuo at 0 °C. The greenish brown solid was cooled to −30 °C, washed with cold isopentane (−30 °C), and dried in vacuo at 0 °C to yield 0.89 g (86%) of analytically pure olive green crystalline $V(CO)_5PPh_3$ (mp 104 °C dec.). Anal. Calcd for $C_{23}H_{15}O_5PV$: C, 60.94; H, 3.34; P, 6.83 (mol wt 453). Found: C, 60.18; H, 3.91; P, 6.54 (mol wt in toluene 436). Infrared spectra in the CO stretching frequency region: (hexane solution) 2052 (m), 1928 (vs) cm^{-1}; (Nujol mull) 2048 (m), 1914 (vs, br) cm^{-1}. Magnetic data (solid state): χ_m^{cor} (at 25 °C) = 1454×10^{-6} cgsu/mol, giving $\mu_{eff} = 1.87\ \mu_B$/mol of vanadium with a diamagnetic correction of 210×10^{-6} cgsu/mol.

$V(CO)_5PPh_3$ is soluble in CH_2Cl_2, toluene, and alkanes to provide orange to yellow solutions which are thermally unstable under vacuum above 0 °C. Also, solid $V(CO)_5PPh_3$ is unstable in the presence of traces of toluene or CH_2Cl_2 and must be completely dry to withstand evacuation at room temperature. Polar solvents such as ether, acetone, and methanol cause decomposition of $V(CO)_5PPh_3$ (vide infra). The solid slowly decomposes under nitrogen at room temperature.

b. From $[Et_4N][V(CO)_5Ph_3P]$ and $[C_7H_7][BF_4]$. Treatment of a mixture of crystalline $[Et_4N][V(CO)_5PPh_3]$[6a] (0.104 g, 0.179 mmol) and $[C_7H_7][BF_4]$ (0.0319 g, 0.179 mmol) with cold (−70 °C) methylene chloride (40 mL) provided a bright yellow solution. An infrared spectrum of the solution at room temperature showed $V(CO)_5PPh_3$ to be the only carbonyl species present (ν(CO) 2050 (m), 1925 (vs) cm^{-1}). No attempts were made to isolate the neutral carbonyl from this reaction.

Reaction of $V(CO)_5Ph_3P$ with Sodium Amalgam. Formation of $[Et_4N][V(CO)_5Ph_3P]$. $V(CO)_5PPh_3$ was prepared in situ by dropwise addition of a cold (−70 °C) toluene solution (20 mL) of PPh_3 (0.59 g, 2.3 mmol) to a toluene slurry (15 mL) of $V(CO)_6$ (0.50 g, 2.3 mmol) at −70 °C. When the solution was warmed to 0 °C, all $V(CO)_6$ dissolved, giving a bright orange solution. An infrared solution spectrum in toluene showed only two bands in the ν(CO) region: 2048 (s), 1910 (vs, br) cm^{-1}, characteristic of $V(CO)_5PPh_3$. An excess of sodium amalgam (0.5% Na by weight; 15 mL) was added. Within minutes a yellow solid began to precipitate. After 12 h of stirring, toluene was removed in vacuo. The resulting solid was dissolved in acetone and metathesized with tetraethylammonium bromide as reported earlier.[6a] A yield of 0.88 g of yellow-orange crystals, identical with genuine $[Et_4N][V(CO)_5PPh_3]$, was obtained (73% yield).

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(3) (a) R. P. M. Werner, *Z. Naturforsch., B*, **16**, 477 (1961); (b) W. Hieber and E. Winter, *Chem. Ber.*, **97**, 1037 (1964).

(4) W. Hieber, E. Winter, and E. Schubert, *Chem. Ber.*, **95**, 3070 (1962).

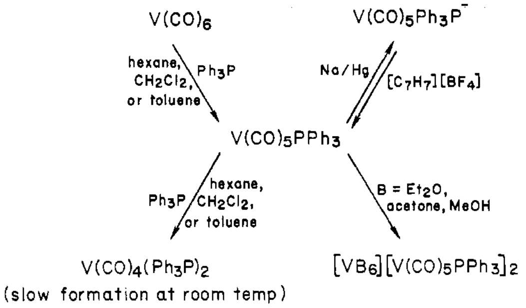
(5) A. M. Bond and R. Colton, *Inorg. Chem.*, **15**, 2039 (1976).

(6) Only photolytically induced substitutions of $V(CO)_6^-$ have been reported: (a) A. Davison and J. E. Ellis, *J. Organomet. Chem.*, **31**, 239 (1971); (b) D. Rehder, *ibid.*, **37**, 303 (1972); (c) J. E. Ellis and R. A. Faltynek, *ibid.*, **93**, 205 (1975); (d) D. Rehder, *J. Magn. Reson.*, **25**, 177 (1977), and references cited therein; (e) M. S. Wrighton, D. I. Handeli, and D. L. Morse, *Inorg. Chem.*, **15**, 434 (1976).

(7) Disproportionation reactions of neutral substituted vanadium carbonyls including $V(CO)_4$diphos (diphos = 1,2-bis(diphenylphosphino)ethane) are discussed by H. Behrens and K. Lutz, *Z. Anorg. Allg. Chem.*, **356**, 225 (1968).

(8) G. Silvestri, S. Gambino, M. Guainazzi, and R. Ercoli, *J. Chem. Soc., Dalton Trans.*, 2558 (1972).

Scheme I. Syntheses and Reactions of (Triphenylphosphine)pentacarbonylvanadium(0)



Results and Discussion

Reactions of Hexacarbonylvanadium with Triphenylphosphine. Werner[3a] and Hieber and Winter[3b] report that the reaction of $V(CO)_6$ with 2 or 3 mol of triphenylphosphine in unreactive solvents for 5 h at room temperature provides orange $V(CO)_4(Ph_3P)_2$. We have found that when the reaction is conducted for shorter periods of time, e.g., for 15 min or less or better at low temperatures, a much more oxygen-, heat-, and solvent-sensitive green compound is obtained in high yields (80–90%). This intermediate product is the paramagnetic monomer $V(CO)_5Ph_3P$ and surprisingly is the first neutral and paramagnetic vanadium carbonyl derivative of the general formula $V(CO)_5L$ to be reported in the scientific literature.

(Triphenylphosphine)pentacarbonylvanadium is formed when 1–3 equiv of triphenylphosphine reacts with hexacarbonylvanadium in hexane, toluene, or methylene chloride. Substitution of $V(CO)_5Ph_3P$ by additional triphenylphosphine is a rather slow process in these solvents at room temperature; e.g., even after 5 h in hexane, a substantial amount of $V(CO)_5Ph_3P$ can be observed in solution by infrared spectroscopy when $V(CO)_6$ is treated with 2 or 3 equiv of Ph_3P.[9] However, attempts to isolate pure $V(CO)_5Ph_3P$ by removing solvent in vacuo at room temperature invariably result in formation of substantial quantities of $V(CO)_4(Ph_3P)_2$. Dry $V(CO)_5Ph_3P$ is stable for short periods at room temperature under vacuum but often suffers rapid decomposition under the same conditions if traces of solvent are present. An independent quantitative synthesis of $V(CO)_5PPh_3$ from the reaction of equimolar amounts of $[Et_4N][V(CO)_5PPh_3]$ and $[C_7H_7][BF_4]$ in methylene chloride at −70 °C also provides support for our formulation. Tropylium ion is often used as a mild and convenient one-electron oxidizing agent to convert carbonyl anions to analogous neutral species.[1]

Analytical (see Experimental Section), magnetic ($\mu_{eff} = 1.87$ μ_B at 25 °C), and infrared data are consistent with the formulation of $V(CO)_5PPh_3$ as a neutral monomeric and paramagnetic derivative of $V(CO)_6$. Infrared spectra of $V(CO)_5PPh_3$ in CH_2Cl_2 show a sharp spike of medium intensity at 2050 cm^{-1} and a rather broad and quite intense absorption at 1925 cm^{-1}. This infrared pattern is very similar to that reported for $Cr(CO)_5PPh_3$[10] except no weak shoulder corresponding to a CO stretch of B_1 symmetry is observed.[11] In impure samples of $V(CO)_5PPh_3$ spikes or shoulders at 1986 and 1954 cm^{-1} due to $V(CO)_4(Ph_3P)_2$ are present in mull spectra.

Reactions of $V(CO)_5Ph_3P$. Scheme I summarizes the reactivity patterns observed for $V(CO)_5PPh_3$. It readily undergoes reduction by sodium amalgam in toluene to provide a 73% yield of crystalline $[Et_4N][V(CO)_5PPh_3]$ and undergoes rapid disproportionation in strong donor solvents such as acetone and methanol to yield $V(CO)_5Ph_3P^-$ as the only carbonyl-containing product. In diethyl ether the reaction requires about 10 min at room temperature before product begins to precipitate[12] and provides the same ether insoluble salt, $[V(Et_2O)_6][V(CO)_5Ph_3P]_2$, that Hieber and Winter[2] obtained by treating $V(CO)_6$ with PPh_3 in ether (eq 1). On this basis, we felt that $V(CO)_5PPh_3$ was a likely intermediate in the unusual reaction reported by Hieber and Winter.[2] By monitoring infrared spectra in the ν(CO) region of the initial stages of this reaction, we have established $V(CO)_5PPh_3$ to be the precursor to $V(CO)_5PPh_3^-$.[13] Thus in this reaction, substitution of $V(CO)_6$ by PPh_3 is significantly faster than the disproportionation of $V(CO)_6$ by diethyl ether since negligible amounts of $V(CO)_6^-$ are generated. In more polar solvents disproportionation reactions of $V(CO)_6$ should compete favorably with substitution reactions. Since these two processes are of central importance to the still poorly understood chemistry of $V(CO)_6$,[1] clearly more (and especially quantitative) data are needed in this area.

To further exclude the possibility that $V(CO)_6^-$ was undergoing substitution by PPh_3 in reaction 1, as suggested earlier,[5] we showed $[V(Et_2O)_6][V(CO)_6]_2$[4] to be inert to PPh_3 in diethyl ether. Previously unreported infrared spectra of this salt are complex in the ν(CO) region in ether solution (1954 (m), 1896 (vs), 1680 (m) cm^{-1}) and in the solid state as a Nujol mull (2034 (mw), 1960 (m), 1944 (m), 1879 (vs), 1686 (s) cm^{-1}) and indicate significant VCO → V interactions are present.[14] Recently, Schneider and Weiss reported the structure of closely related $[V(THF)_4][V(CO)_6]_2$ which shows an isocarbonyl interaction.[15] However, in this case it is evidently a sufficiently weak interaction to have surprisingly little effect on the carbonyl stretching frequencies of the anion. Only one band at 1850 cm^{-1} is reported to be present in the ν(CO) region for a mull spectrum of $[V(THF)_4][V(CO)_6]_2$. A strong isocarbonyl interaction should labilize terminal carbonyl groups while strengthening the V–C bond of the bridging carbonyl. Clearly this labilizing effect for $[V(Et_2O)_6][V(CO)_6]_2$ is too weak to permit thermal substitution of $V(CO)_6^-$ by triphenylphosphine at room temperature. However, other Lewis acids which have more affinity for the carbonyl oxygen than

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(9) Interestingly, the purification step used by Werner[3a] and Hieber and Winter[3b] to isolate $V(CO)_4(Ph_3P)_2$ involves the use of methanol which immediately disproportionates $V(CO)_5Ph_3P$ to soluble $[V(MeOH)_n][V(CO)_5Ph_3P]_2$, leaving insoluble $V(CO)_4(Ph_3P)_2$. It is possible that the methanol treatment used in the isolation of other $V(CO)_4(R_3P)_2$[3b] (R = alkyl, H) also destroyed corresponding $V(CO)_5(R_3P)$ species.

(10) T. A. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz, *J. Am. Chem. Soc.*, **83**, 3200 (1961).

(11) P. S. Braterman, "Metal Carbonyl Spectra", Academic Press, London, 1975.

(12) Reaction conditions: 250 mg of $V(CO)_5PPh_3$ dissolved in 20 mL of diethyl ether at room temperature. Some unreacted $V(CO)_5PPh_3$ remains in solution even after 5 h as evidenced by bands in the ν(CO) region at 2050 (w) and 1925 (s) cm^{-1}. Very weak spikes at 1898, 1865 1677, 1643, and 1636 cm^{-1} are also observed in ether. Previously unreported mull spectra of $[V(Et_2O)_6][V(CO)_5PPh_3]_2$ are complex in the ν(CO) region: 1888 (m), 1840 (vs), 1713 (w), 1665 (sh), 1658 (s) cm^{-1}. In very polar solvents such as diglyme or hexamethylphosphoramide the spectra simplify to the usual three band pattern characteristic of unperturbed $V(CO)_5PPh_3^-$.[6a] Clearly V–CO → V interactions are likely to be present in the solid salt. Similar complex spectra are observed for $[V(Et_2O)_6][V(CO)_6]_2$ (vide infra).

(13) Reaction conditions: To a cold (−70 °C) mixture of 0.627 g (2.86 mmol) of $V(CO)_6$ and 2.25 g (8.59 mmol) of PPh_3 was added 40 mL of cold (−70 °C) diethyl ether. Over a period of 2 h the stirred slurry warmed to 0 °C. An infrared spectrum taken at this time showed $V(CO)_5PPh_3$ to be the only carbonyl species in solution. A small amount of unreacted solid $V(CO)_6$ was also present at this time. After 14 h of stirring at room temperature, yellow powdery $[V(Et_2O)_6][V(CO)_5PPh_3]_2$ was removed by filtration and dried (yield 0.79 g, 20%). No infrared bands attributable to $[V(Et_2O)_6][V(CO_6]_2$ were observed in the solid or in solution.

(14) In very polar solvents such as hexamethylphosphoramide (HMPA), $[V(Et_2O)_6][V(CO)_6]_2$ and $[Et_4N][V(CO)_6]$ have identical infrared spectra in the ν(CO) region, one very intense absorption at 1860 cm^{-1} which is expected for unperturbed $V(CO)_6^-$. HMPA is effective in minimizing anion perturbation caused by ion pairing effects (cf. J. E. Ellis and G. P. Hagen, *J. Am. Chem. Soc.*, **96**, 7825 (1974)).

(15) M. Schneider and E. Weiss, *J. Organomet. Chem.*, **121**, 365 (1976).

$[V(Et_2O)_{6-n}]^{2+}$ could possibly be used to catalyze such substitution reactions.

Conclusion

Hexacarbonylvanadium(0) reacts with 1 or more equiv of triphenylphosphine in hexane, toluene, or methylene chloride to provide high yields of (triphenylphosphine)pentacarbonylvanadium, a monomeric, paramagnetic ($\mu_{eff} = 1.87$ μ_B), and base-sensitive nonelectrolyte. This first example of a neutral monosubstituted pnicogen derivative of $V(CO)_6$ is also obtained from the oxidation of $[(C_2H_5)_4N][V(CO)_5PPh_3]$ with 1 equiv of tropylium fluoroborate.

(Triphenylphosphine)pentacarbonylvanadium(0) readily undergoes disproportionation in ethereal and more polar solvents to yield $V(CO)_5PPh_3^-$ as the only carbonyl-containing species. It has been established that the reaction of $V(CO)_6$ and triphenylphosphine in diethyl ether, originally reported by Hieber and Winter to form $[V(Et_2O)_6][V(CO)_5PPh_3]_2$, proceeds via the intermediate formation of $V(CO)_5PPh_3$. Thus, in this system, $V(CO)_6$ undergoes substitution by PPh_3 considerably faster than it is disproportionated by diethyl ether.

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Registry No. $[Et_4N][V(CO)_6]$, 56328-27-9; $V(CO)_6$, 14024-00-1; $V(CO)_5Ph_3P$, 72622-82-3; $[Na(diglyme)_2][V(CO)_6]$, 15531-13-2; $[Et_4N][V(CO)_5Ph_3P]$, 10170-61-3; $[V(Et_2O)_6][V(CO)_5PPh_3]_2$, 72622-84-5.

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Evaluation of 1,4-Dicyanobenzene as a New Internal Standard in Utilizing Solid-State Infrared Intensity Methods for the Determination of Thiocyanate Bonding Modes

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Although a wide variety of instrumental techniques[2-7] have been utilized as diagnostic tools in the determination of the bonding modes of ambidentate ligands, infrared spectroscopy[8] has proved to be the most useful, especially for thiocyanate. Despite a few inherent difficulties, the ν_{CN} bands of coordinated thiocyanate provide the most definitive criteria in this respect, in terms of their integrated absorption intensities.[8] When measured in the same solvent, these intensities vary in the order M–SCN < NCS⁻ < M–NCS, regardless of gross complex geometry. The use of an internal standard,[9] specifically salicylic acid, has facilitated the determination of relative ν_{CN} integrated intensity ratios, otherwise known as internal standard ratios (ISR), in the solid state.

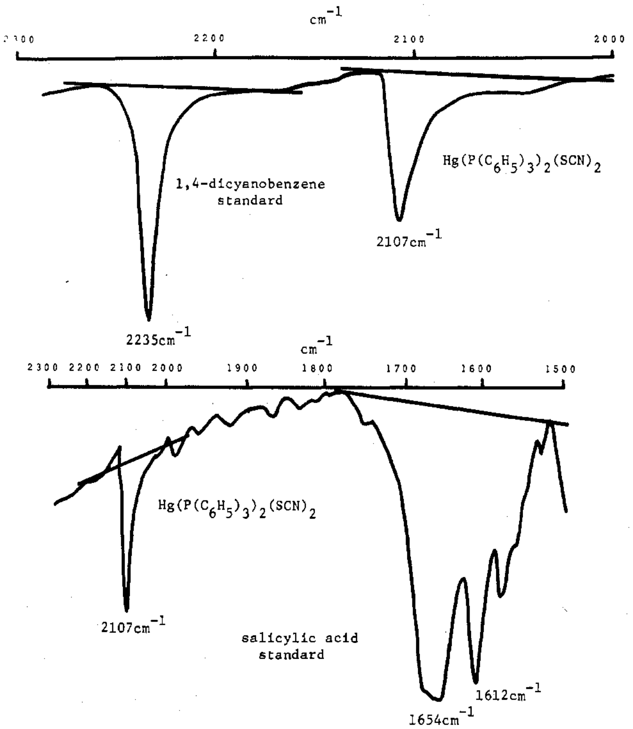

Figure 1. Representative spectra of complex and standards: upper, 1,4-dicyanobenzene standard and (dithiocyanato)bis(triphenylphosphine)mercury(II); lower, (dithiocyanato)bis(triphenylphosphine)mercury(II) and salicylic acid standard.

The previously published ISR values (see, for example, ref 8–11) have fallen into two ranges which parallel the intensity data obtained for solutions (M–SCN, <1; M–NCS, >1.5). However, the peaks in the ν_{CO} region of salicylic acid which have been used as standards (1654 cm^{-1},[8,9,11] 1612 cm^{-1} [10]) are quite irregular, making the evaluation of relative areas subject to considerable uncertainty. Furthermore, they occur in a region of the spectrum which is coincident with the absorption bands of many organic ligands. In addition, it has been shown[2,3] that the thiocyanate's bonding mode can be influenced by the surrounding environment, i.e., counterions, solvent, and physical state. Salicylic acid has the potential to significantly interact with the thiocyanate ion. Noteworthy shifts in the ν_{CN} frequencies of coordinated thiocyanates have, in fact, been observed[12,13] in the presence of salicylic acid. This, coupled with the aforementioned difficulties in evaluating relative peak areas, prompted us to search for a new internal standard. As is documented in the following discussion, we

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