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Registry No. Ru(bpy)$_2$(**1**)(PF$_6$)$_2$, 77744-81-1; Ru(bpy)(**1**)$_2$(PF$_6$)$_2$, 77744-83-3; Ru(bpy)$_2$(**2**)(PF$_6$)$_2$, 77773-65-0; Ru(bpy)$_2$(**3**)(PF$_6$)$_2$, 77744-85-5; Ru(bpy)$_2$Cl$_2$, 19542-80-4; Ru(bpy)Cl$_3$, 69141-04-4; Ru(bpy)$_3$$^{2+}$, 15158-62-0; 1,2-diaminobenzene, 95-54-5; 1,2-diaminonaphthalene, 938-25-0; 9,10-diaminophenanthrene, 53348-04-2.

Supplementary Material Available: A listing of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

Notes

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η^5-(Triphenylphosphonium cyclopentadienylide)rhodium(I) and -rhodium(III) Complexes

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In connection with our current interest concerning the formation and chemical reactivity of new (η^5-cyclopentadienyl)rhodium and -iridium organometallic complexes,[2] we have investigated the reactions of triphenylphosphonium cyclopentadienylide (**1**) with some rhodium(I) and rhodium(III) substrates. The interest for such a study arises from the fact that, in the ground state, **1** is considered to be the resonance hybrid of ylidic and ylenic structures with a predominant contribution of the former. Coordination to metals by the ylidic structure implies that the five-membered ylide ring is a 6π-electron donor, as the cyclopentadienyl ion. It is, therefore, of interest to compare the properties of some of the new complexes with that of analogous cyclopentadienylrhodium(I) and -rhodium(III) complexes.

Experimental Section

Triphenylphosphonium cyclopentadienylide (**1**)[3] and the complexes [Rh(CO)$_2$Cl]$_2$,[4] [Rh(1,5-C$_8$H$_{12}$)Cl]$_2$,[5] [Rh(C$_7$H$_8$)Cl]$_2$,[6] and [Rh(C$_5$Me$_5$)Cl$_2$]$_2$[7] were prepared by literature methods. Other reagents were commercial products and were used without purification. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer in KBr pellets. Proton NMR spectra were recorded by using a Perkin-Elmer R 24B spectrometer. ^{13}C NMR spectra were recorded in 10-mm tubes at a probe temperature of 303 K on a Bruker WP-80 FT spectrometer working at 20.1 MHz and using ca. 10% (w/v) solutions containing tetramethylsilane (Me$_4$Si) as internal reference. The carbon spectra were recorded in the quadrature detection mode with use of a pulse angle of 20° and a pulse delay equal to the dwell time on 8192 (8 K) data points. Off-resonance decoupling experiments were carried out with the proton frequency offset approximately 500 Hz downfield from the center of the proton spectra region. Conductivity measurements were made with a WTW LBR conductivity meter.

Microanalyses were done by the laboratory of the Organic Chemistry Institute of Milan. All the reactions were carried out under an atmosphere of oxygen-free nitrogen. Analytical data, characteristic IR bands, and ^{1}H and ^{13}C NMR absorptions are reported in Tables I and II.

[Rh(Ph$_3$PC$_5$H$_4$)(CO)$_2$]PF$_6$ (2). To a stirred acetone solution of [Rh(CO)$_2$Cl]$_2$ (0.21 g) were added solid Ph$_3$PC$_5$H$_4$ (0.32 g) and Ag[PF$_6$] (0.25 g). The initial red solution changed to pale brown while AgCl precipitate was formed. After 40 min solid AgCl was separated by filtration, and the solvent was removed by evaporation. The solid was dissolved in 10 mL of CH$_2$Cl$_2$, and diethyl ether was added to precipitate the product as a yellow brown solid. The yield was 85%.

[Rh(Ph$_3$PC$_5$H$_4$)(1,5-C$_8$H$_{12}$)]PF$_6$ (3). Solid Ph$_3$PC$_5$H$_4$ (0.414 g) and Ag[PF$_6$] (0.32 g) were added to a stirred acetone solution of [Rh(1,5-C$_8$H$_{12}$)Cl]$_2$ (0.31 g). The reaction mixture was left with stirring, at room temperature, for ca. 2 h. The AgCl precipitate formed was separated by filtration and the resulting solution evaporated. The crude product was dissolved in 10 mL of CH$_2$Cl$_2$; with addition of diethyl ether a yellow brown solid was formed. This was collected, washed with diethyl ether, and dried. The yield was 82%.

[Rh(Ph$_3$PC$_5$H$_4$)(C$_7$H$_8$)]PF$_6$ (4). This compound was prepared in the same manner as **3**, starting from [Rh(C$_7$H$_8$)Cl]$_2$. The yield was 80%.

[Rh(Ph$_3$PC$_5$H$_4$)(CO)PPh$_3$]PF$_6$ (5). To a dichloromethane solution of (**2**) (0.12 g) was added a slight excess of PPh$_3$ (0.052 g). The reaction was monitored by IR spectra and was allowed to proceed until the ν(CO) due to the starting complex had completely disappeared (ca. 2 days). With addition of petroleum ether a brown solid was formed; this was collected, washed with petroleum ether, and dried. The yield was 92%.

Tetraphenylborate Salts. Tetraphenylborate salts of complexes **2–5** were prepared by adding Na[BPh$_4$] dissolved in methanol to a solution of the hexafluorophosphate salts **2–5** in the same solvent. They closely resemble the corresponding PF$_6$$^-$ salts except for lower solubility in organic solvents.

[(Ph$_3$PC$_5$H$_4$)(CO)Rh(μ-Ph$_2$PCH$_2$PPh$_2$)Rh(CO)(Ph$_3$PC$_5$H$_4$)][PF$_6$]$_2$ (6). To a dichloromethane solution of (**2**) (0.13 g) was added Ph$_2$PCH$_2$PPh$_2$ (0.042 g) and the mixture vigorously stirred at room temperature until the ν(CO) due to the starting material had completely disappeared (ca. 5 days). With addition of diethyl ether the product was obtained as a brown solid; this was collected, washed with diethyl ether, and dried. The yield was 82%.

{(Ph$_3$PC$_5$H$_4$)(CO)Rh[μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$]Rh(CO)(Ph$_3$PC$_5$H$_4$)}[PF$_6$]$_2$ (7). This compound was prepared by a method analogous to that given above. The product was recrystallized once from dichloromethane–diethyl ether, giving the pure compounds in 76% yield.

[Rh(C$_5$Me$_5$)(Ph$_3$PC$_5$H$_4$)][PF$_6$]$_2$ (8). To an acetone solution of [Rh(C$_5$Me$_5$)(acetone)$_3$][PF$_6$]$_2$, obtained from [Rh(C$_5$Me$_5$)Cl$_2$]$_2$ (0.45 g) and Ag[PF$_6$], was added Ph$_3$PC$_5$H$_4$ (0.36 g), and the mixture was stirred for 2 h. The initial yellow changed to brown. After filtration the solvent was evaporated off and the crude product dissolved in dichloromethane; with addition of diethyl ether the product was obtained as a yellow-brown solid. The yield was 78%.

Results and Discussion

Triphenylphosphonium cyclopentadienylide (**1**) is a poor nucleophile toward rhodium(I) substrates; this is shown by the lack of chloro bridge-splitting reactions with the binuclear complexes [Rh(CO)$_2$Cl]$_2$, [Rh(1,5-C$_8$H$_{12}$)Cl]$_2$, and [Rh(C$_7$H$_8$)Cl]$_2$. The route followed for the preparation of (triphenylphosphinium cyclopentadienylide)rhodium(I) complexes involves the in situ formation of solvento species from the dimeric chloro-bridged complexes and the displacement of the

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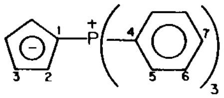
Table I. Analytical, IR, and Proton NMR Data

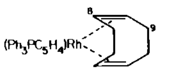
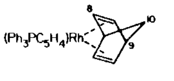
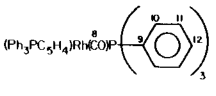
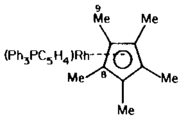
compd	% C calcd	% C found	% H calcd	% H found	IR[a] ν(CO), cm^{-1}	^{1}H NMR $\delta(C_5H_4)$[b,c]	^{1}H NMR $\Delta\delta$[d]
$[Rh(Ph_3PC_5H_4)(CO)_2]PF_6$ (2)	47.64	47.58	3.04	3.09	2067, 2018	6.04, 5.57	0.47
$[Rh(Ph_3PC_5H_4)(1,5\text{-}C_8H_{12})]PF_6$ (3)	54.56	54.52	4.58	4.56		5.86, 4.92	0.94
$[Rh(Ph_3PC_5H_4)(C_7H_8)]PF_6$ (4)	54.07	54.11	4.08	4.12		5.78, 4.94	0.84
$[Rh(Ph_3PC_5H_4)(CO)PPh_3]PF_6$ (5)	58.35	58.46	3.96	4.05	1969	5.77, 4.92	0.85
$\{[Rh(Ph_3PC_5H_4)(CO)]_2(\mu\text{-dppm})\}[PF_6]_2$ (6)	55.18	55.07	3.80	3.80	1983	5.74, 4.88	0.86
$\{[Rh(Ph_3PC_5H_4)(CO)]_2(\mu\text{-dppb})\}[PF_6]_2$ (7)	55.96	55.84	4.08	4.13	1967	5.78, 4.90	0.88
$[Rh(Ph_3PC_5H_4)(C_5Me_5)][PF_6]_2$ (8)	46.38	46.41	4.01	4.06		6.25[e,f]	0.00

[a] Nujol mull. All absorptions are very strong. [b] $CDCl_3$ solution except as noted. [c] α and β protons are indistinguishable and are observed as multiplets. [d] Difference between α and β protons chemical shift in ppm. [e] $Me_2SO\text{-}d_6$ solution. [f] $\delta(C_5Me_5)$ 1.88 (s).

Table II. ^{13}C Chemical Shifts[a] of Triphenylphosphonium Cyclopentadienylide (1) and of Its Complexes with Rhodium Derivatives



1

compd[c]	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12
$Ph_3PC_5H_4$ (1)	80.3[b]	116.3 (J_{CP} = 15.8)	114.2 (J_{CP} = 17.7)	126.3 (J_{CP} = 92.5)	133.4 (J_{CP} = 9.8)	129.4 (J_{CP} = 11.8)	131.6 (J_{CP} = 9.8)					
$(Ph_3PC_5H_4)Rh(\overset{8}{C}O)_2$ (2)	83.1 (J_{CP} = 100, $J_{C\text{-}Rh}$ = 6.2)	97.9 (J_{CP} = 11.8, $J_{C\text{-}Rh}$ = 3.9)	93.8 (J_{CP} = 13.8, $J_{C\text{-}Rh}$ = 3.9)	119.3 (J_{CP} = 94.5)	134.1 (J_{CP} = 11.8)	130.4 (J_{CP} = 13.8)	135.4 (J_{CP} = 2)	187.9 ($J_{C\text{-}Rh}$ = 84.6)				
 (3)	75.8 (J_{CP} = 110, $J_{C\text{-}Rh}$ = 5.2)	96.4 (J_{CP} = 11.8, $J_{C\text{-}Rh}$ = 3.9)	91.5 (J_{CP} = 14.0, $J_{C\text{-}Rh}$ = 3.9)	120.3 (J_{CP} = 92.5)	133.8 (J_{CP} = 9.9)	130.3 (J_{CP} = 11.8)	135.2 (J_{CP} = 3.9)	68.1 ($J_{C\text{-}Rh}$ = 11.8)	31.2			
 (4)	75.9 (J_{CP} = 106.4, $J_{C\text{-}Rh}$ = 6.2)	93.8 (J_{CP} = 11.8, $J_{C\text{-}Rh}$ = 3.9)	90.3 (J_{CP} = 13.8, $J_{C\text{-}Rh}$ = 3.9)	120.7 (J_{CP} = 92.5)	133.9 (J_{CP} = 9.8)	130.4 (J_{CP} = 11.8)	135.3 (J_{CP} = 2)	32.2 ($J_{C\text{-}Rh}$ = 9.8)	57.9 ($J_{C\text{-}Rh}$ = 7.9)	46.0 ($J_{C\text{-}Rh}$ = 0)		
 (5)	79.9[b]	97.0 (J_{CP} = 11.8, $J_{C\text{-}Rh}$ = 3.9)	92.8 (J_{CP} = 13.8, $J_{C\text{-}Rh}$ = 3.9)	120.6 (J_{CP} = 98.5)	133.8 (J_{CP} = 11.9)	129.5 (J_{CP} = 13.8)	135.2	b	135.5 (J_{CP} = 17.8)	133.2 (J_{CP} = 11.8)	130.8 (J_{CP} = 9.8)	128.6
 (8)	81.3 (J_{CP} = 94.5, $J_{C\text{-}Rh}$ = 6)	96.1 (J_{CP} = 9.8, $J_{C\text{-}Rh}$ = 5.9)	93.8 (J_{CP} = 11.8, $J_{C\text{-}Rh}$ = 5.9)	117.2 (J_{CP} = 90.6)	134.1 (J_{CP} = 11.8)	131.0 (J_{CP} = 13.8)	136.3 (J_{CP} = 2)	104.0 ($J_{C\text{-}Rh}$ = 7.9)	9.9			

[a] Spectra were recorded at 30 °C on ca. 10% (w/v) solutions in dimethyl-d_6 sulfoxide which also provided the deuterium lock; chemical shifts are reported in ppm downfield from Me_4Si, the values of the coupling constants are in Hz. [b] Signal to noise insufficient for assignment. [c] Only the cationic counterpart is reported.

coordinated solvent by **1**. The reactions occur rapidly at room temperature, and high yields of the product can be obtained, particularly by use of acetone as solvent. Thus, treatment of acetone solutions of $[Rh(CO)_2Cl]_2$, $[Rh(1,5\text{-}C_8H_{12})Cl]_2$, or $[Rh(C_7H_8)Cl]_2$ with $Ag[PF_6]$ and **1** in acetone solution gives $[Rh(Ph_3PC_5H_4)(CO)_2]PF_6$ (**2**), $[Rh(Ph_3PC_5H_4)(1,5\text{-}C_8H_{12})]PF_6$ (**3**), or $[Rh(Ph_3PC_5H_4)(C_7H_8)]PF_6$ (**4**). These complexes, which are also obtained as tetraphenylborate salts, are very stable in the solid state and in solution but decompose slowly in solution by heating; they are insoluble in diethyl ether and benzene, slightly soluble in dichloromethane and methanol, and fairly soluble in acetone and dimethyl sulfoxide.

In complex **2** the $\nu(CO)$ are observed at higher wavenumbers than in the corresponding η^5-cyclopentadienyl complex; this suggests that **1** is more electron withdrawing than cyclopentadienyl ion also if the effect of the charge on the complex on the $\nu(CO)$ must be considered.

In the ^1H NMR spectra of complexes **2–4** proton resonances of the cyclopentadienylide ring are observed in the form of two multiplets, assignable to α and β protons, shifted upfield as compared with free **1**. The chemical shift difference between α and β protons in complexes **2–4** is very different. This difference, in fact, in complex **2** is comparable with that found for other cyclopentadienylide metal complexes[8-12] but in complexes **3** and **4** is much greater (Table I). The coordinated double bonds in complexes **3** and **4** can give rise to anisotropy effects which are likely to be responsible for the chemical shift difference between the α and β protons. The single-crystal X-ray diffraction of the tetraphenylborate salt of **3** is presently being studied.[13]

The most conclusive information on the effect of coordination upon the properties of **1** is obtained from the ^{13}C NMR spectra. Assignment of resonances in the proton noise fully decoupled spectra was usually straightforward. Ambiguities were resolved, when possible, by off-resonance experiments and by comparison with each other and with known ^{13}C chemical shifts of closely related molecules.[14] The resonances due to the carbon atoms bound directly to phosphorus appear as relatively low-intensity signals with large coupling constants. The chemical shifts and the $^{13}C-^{31}P$ nuclear spin couplings of **1**, although measured in a different solvent (Me_2SO), are very close to those already reported in the literature.[15] The ambient-temperature ^{13}C NMR spectra of compounds **2–4** show only one set of signals for the carbons labeled C-8 in Table II. This finding demonstrates the fluxional behavior of the complexes where the triphenylphosphonium cyclopentadienylide moiety is free to rotate around its bond with the rhodium. This fact is also confirmed by the examination of the values of the spin–spin coupling constants between ^{103}Rh and ^{13}C which are large for the CO moiety in compounds **2**[16] but rather small for the carbons of the olefinic ligands, as already observed in analogous cyclopentadienyl derivatives.[14]

Examination of Table II reveals that the chemical shifts of carbons C-1, C-2, C-3, and C-4 experience a substantial upfield shift upon complexation with rhodium when compared with the corresponding ones of the free ligand; on the other hand, these chemical shifts do not vary appreciably within the series of complexes investigated.

Therefore ^{13}C NMR chemical shift data indicate[10,12,15] that in the prepared complexes the ligand (**1**) is coordinated to rhodium atom in the ylidic form.

Of particular relevance is the upfield shift of the olefinic carbons C-8 in compounds **3** and **4** upon complexation. In fact, these resonances fall in the region where one would expect the resonances of saturated carbon atoms, indicating an increase in s character of the rhodium–olefin–carbon bond. The upfield shift of the carbons C-8 in compound **4** is $\Delta\delta = 143.9 - 32.2 = +111.7$ ppm, whereas in compounds **5** this upfield shift is $\Delta\delta = 127.8 - 68.5 = +59.7$ ppm.[17]

We have investigated the reactions of **2** with some nucleophiles. Dichloromethane solutions of **2** react easily, at room temperature, with $[Ph_4As]Cl$ or C_5H_5Tl to give respectively the complexes $[Rh(CO)_2Cl_2]AsPh_4$[18] and $[Rh(C_5H_5)(CO)_2]$.[19] Both products obtained were identified by comparison with authentic samples. In these reactions occurs substitution of ligand **1** by chloride or cyclopentadienyl ion instead of the carbonyl groups. An inspection of the spectral changes in the $\nu(CO)$ region occurring during the reactions clearly indicates that no intermediates are present at detectable concentration.

Compound **2** reacts with PPh_3, at room temperature, to give $[Rh(Ph_3PC_5H_4)(CO)PPh_3]PF_6$ (**5**) as a yellow-brown solid, slightly soluble in CH_3OH and CH_2Cl_2 and soluble in acetone and dimethyl sulfoxide. The reaction requires very mild conditions with respect to those necessary in the analogous reaction of $[Rh(C_5H_5)(CO)_2]$.[20] A kinetic study has shown that $[Rh(C_5H_5)(CO)_2]$ reacts with tertiary phosphines by an S_N2 mechanism involving a dipolar transition state.[20] On the assumption that the reaction of **2** with PPh_3 occurs by a similar mechanism, the milder conditions required with respect to the analogous reaction of $[Rh(C_5H_5)(CO)_2]$ may suggest that the dipolar transition state is more accessible for **1** than for $C_5H_5^-$.

In the proton NMR spectrum of **5** the chemical shift difference between the α and β protons of **1** is greater than in the corresponding dicarbonyl (**2**) and is comparable to those observed for complexes **3** and **4**. In this case the large chemical shift difference could be partially due to the anisotropy of **1** on the PPh_3 ligand.

We have also studied the reactions of **2** with the chelating diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 1, 2, 4$). On the basis of the steric property of the ligand dppm (dppm = $Ph_2PCH_2PPh_2$), which commonly acts as a bridging ligand,[21] the formation of the dimeric dicationic rhodium(I) complex $[(Ph_3PC_5H_4)(CO)Rh(\mu\text{-dppm})Rh(CO)(Ph_3PC_5H_4)][PF_6]_2$ (**6**) from the reaction of **2** with dppm was expected. The reaction product of **2** with dppb (dppb = $Ph_2P(CH_2)_4PPh_2$), $[(Ph_3PC_5H_4)(CO)Rh(\mu\text{-dppb})Rh(CO)(Ph_3PC_5H_4)][PF_6]_2$ (**7**), is also a binuclear dicationic complex of rhodium(I) containing the diphosphine bridging two metal atoms. As far as rhodium(I) complexes are concerned, both compounds in which dppb acts as a bridging ligand and compounds in which dppb behaves as a chelating ligand are known.[22] Displacement of

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1 and of the carbonyl ligands occurs in the reaction of **2** with dppe (dppe = $Ph_2PCH_2CH_2PPh_2$), and the product is the known $[Rh(dppe)_2]PF_6$. In the formation of **6** and **7** an excess of ligand must be avoided. Complexes **6** and **7** are air stable, yellow-brown solids, soluble in acetone and chlorinated solvents; their conductivities, in acetone solution, are in the range found for 1:2 electrolytes. Apart from the shift in the carbonyl stretching frequency, the IR spectra of **6** and **7** closely resemble the spectrum of **5**. The proton NMR spectra of **6** and **7** show a chemical shift difference between α and β protons of ligand **1** comparable with that of complex **5**. By analogy to **3–5** we assume these complexes (**1**) are η^5-coordinated.

The solvento complex $[Rh(C_5Me_5)(acetone)_3][PF_6]_2$[23] easily reacts with **1** to give the sandwich-type rhodium(III) complex $[Rh(C_5Me_5)(Ph_3PC_5H_4)][PF_6]_2$ (**8**) as a yellow-brown solid. In the proton NMR spectrum of **8** the resonances of α and β protons of coordinated $Ph_3PC_5H_4$ are not distinguishable since they are split into a multiplet at τ 3.78. A zero chemical shift difference between α and β protons was observed[24] for the cationic complex $[Pd(\eta^3\text{-allyl})(Ph_3PC_5H_4)]BF_4$, and the chemical shift difference of the α and β protons in the ananlogous $[Pd(\eta^3\text{-}Ph_3PC_3H_4)(Ph_3PC_5H_4)][BF_4]_2$ was attributed to an anisotropy of the phenyl rings on the triphenylphosphonium allylide ligand. The high formal oxidation state of the metal in complex **8** probably determines the lack of difference in the chemical shift. However, the ^{13}C NMR chemical shifts of **8** fall in the range of the described complexes; the major difference is observed, as expected, in the values of the coupling constants between ^{103}Rh and ^{13}C.

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Registry No. **1**, charged form, 29473-30-1; **1**, uncharged form, 2224-32-0; **2**, PF_6 salt, 77589-85-6; **2**, BPh_4 salt, 77589-86-7; **3**, PF_6 salt, 77589-88-9; **3**, BPh_4 salt, 77589-89-0; **4**, PF_6 salt, 77589-91-4; **4**, BPh_4 salt, 77589-92-5; **5**, PF_6 salt, 77589-94-7; **5**, BPh_4 salt, 77589-95-8; **6**, 77589-97-0; **7**, 77611-44-0; **8**, 77589-99-2; $[Rh(CO)_2Cl]_2$, 14404-25-2; $[Rh(1,5\text{-}C_8H_{12})Cl]_2$, 12092-47-6; $[Rh(C_7H_8)Cl]_2$, 12257-42-0; $[Rh(C_5Me_5)Cl_2]_2$, 12354-85-7; $[Rh(C_5Me_5)(acetone)_3][PF_6]_2$, 60936-90-5.

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Synthesis and Structure of Hexakis(*tert*-butyl isocyanide)vanadium(II) Hexacarbonylvanadate(–I)

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We recently reported the synthesis of $[V(CN\text{-}t\text{-}Bu)_6]^{2+}$ by reduction of vanadium(III) chloride in ethanol.[1] The hexafluorophosphate salt of this homoleptic vanadium isocyanide complex was characterized by elemental analysis and infrared spectroscopy. In the present study, the $[V(CN\text{-}t\text{-}Bu)_6]^{2+}$ cation was obtained from $[V(CO)_6]^-$ by oxidation and addition of *tert*-butyl isocyanide. This convenient new route parallels that used previously[2] to obtain the homoleptic seven-coordinate isocyanide complexes of molybdenum(II) and tungsten(II). We also describe the crystal and molecular structure of $[V(CN\text{-}t\text{-}Bu)_6][V(CO)_6]_2$.

Experimental Section and Results

Synthetic Work. All compounds were handled under an atmosphere of dry nitrogen with use of Schlenk techniques or in a Vacuum Atmosphere drybox. *tert*-Butyl isocyanide,[3] tetraethylammonium hexacarbonylvanadate(–I),[4] trichlorotris(*tert*-butyl isocyanide)vanadium(III),[1] and iodobenzene dichloride ($PhICl_2$)[5] were prepared by literature methods. All other starting materials were commercially available. Solvents were distilled from appropriate drying agents under nitrogen and degassed immediately before use. Chemical analyses were performed by Galbraith Laboratories, Knoxville, Tn.

Preparation of Hexakis(*tert*-butyl isocyanide)vanadium(II) Hexacarbonylvanadate(–I). Method 1. A slurry of 1.1 g (3.1 mmol) of tetraethylammonium hexacarbonylvanadate(–I) in 15 mL of ethanol and 5 mL (48 mmol) of *tert*-butyl isocyanide was combined with a slurry of 0.473 g (1.72 mmol) of iodobenzene dichloride in 15 mL of ethanol. A vigorous reaction occurred with the evolution of gas, and the product precipitated as an orange solid. The reaction mixture was stirred until all of the yellow, solid tetraethylammonium hexacarbonylvanadate(–I) was consumed (0.5 h). The crude product was collected by filtration, washed with a small volume of ethanol, and vacuum-dried. The product was recyrstallized from 10 mL of methylene chloride by layering on 20 mL of diethyl ether. The yield of red crystalline product was 0.73 g (73%). Anal. Calcd for $C_{42}H_{54}N_6O_{12}V_3$: C, 51.07; H, 5.51; N, 8.51; O, 19.44; V, 15.47. Found: C, 51.16; H, 5.69; N, 8.50; O, 19.33 (by difference); V, 15.32. IR (Nujol mull): 2197 (s), 1850 (s, br), 1235 (w), 1200 (m), 1020 (w), 850 (w), 655 (s), 520 (w), 455 (w) cm^{-1}. ^1H NMR in CD_2Cl_2 vs. Me_4Si: δ 5 ($\Delta\nu_{1/2}$ = 250 Hz).

Method 2. A solution containing 0.20 g (0.49 mmol) of trichlorotris(*tert*-butyl isocyanide)vanadium(III) in 6 mL of ethanol and 4 mL (38 mmol) of *tert*-butyl isocyanide was syringed onto 0.37 g (1.1 mmol) of solid tetraethylammonium hexacarbonylvanadate(–I). The product precipitates as the tetraethylammonium hexacarbonylvanadate(–I) dissolves. Hexakis(*tert*-butyl isocyanide)vanadium(II) hexacarbonylvanadate(–I) (0.18 g, 38%) was collected by filtration and identified by its color, solubilty properties, and infrared spectrum.

Crystallographic Work. While crystals of $[V(CN\text{-}t\text{-}Bu)_6][V(CO)_6]_2$ could be examined briefly in air, diffracted intensity was lost over periods of hours or days unless the most scrupulous care was taken to exclude air at all stages. Crystals used in the structure determination were selected and mounted under an atmosphere of nitrogen in a glovebag containing P_2O_5 to scavenge water and freshly reduced BASF catalyst to scavenge oxygen. Crystals were pushed into 0.5-mm thin-walled glass capillary tubes which had been prepurged in a drybox and were held in place with silicone grease. A first set of data was collected with use of graphite-monochromated Mo K$\bar{\alpha}$ radiation. Intensities from this crystal fell off rapidly at higher scattering angles, and data could be gathered only

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