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Lithium Incorporation by Vanadium Pentoxide

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Treatment of solid V_2O_5 with a solution of lithium iodide in acetonitrile at room temperature affords a series of bronzes, $Li_xV_2O_5$ ($0 < x \leq 1.0$), distinct from those with the same composition prepared above 300 °C. The structures of these bronzes appear to be closely related to that of V_2O_5. In these bronzes V_2O_5 acts as a three-dimensional framework host for lithium. Magnetic susceptibility, X-ray powder diffraction, and DSC data for the bronzes are reported.

The potential for mixed valence and variable composition in bronzes of transition-metal oxides has generated interest in the study of their chemistry and electronic properties.[1] Most alkali metal bronzes, A_xMO_y, have been prepared at high temperatures. If diffusion of A into the crystal lattice of MO_y is sufficiently rapid, electrical energy may be obtained by the electrochemical formation of the bronze in a galvanic cell with an anode A, a cathode MO_y, and an electrolyte containing A^+.[2] Various metal oxides have been shown to form bronzes in electrochemical cells with Li anodes at room temperature, including those of vanadium,[2,3] molybdenum,[2,4,5] and chromium.[6] The reversibility of this bronze formation allows many of these cells to be rechargeable. Charging the cells regenerates the metal oxide and replates Li onto the anode.

Bronzes of V_2O_5 with Li, $Li_xV_2O_5$ ($0 < x \leq 1$), prepared at 650 °C have been previously characterized.[7-11] Walk[12] suggested intercalation of Li in V_2O_5 as the mechanism of the cathodic reaction in $Li/Li^+/V_2O_5$ cells, and Whittingham[2] presented evidence that the bronze formed in these cells is distinct from that formed at high temperatures. In this paper we report the preparation and characterization of $Li_xV_2O_5$ ($0 < x \leq 1$) bronzes formed at room temperature by treatment of V_2O_5 with a solution of lithium iodide in acetonitrile. These new bronzes are closely related to V_2O_5 and convert to the previously reported $Li_xV_2O_5$ bronzes above 300 °C.

Experimental Section

The V_2O_5 used was prepared from reagent grade (Alfa) NH_4VO_3;[13] reagent grade acetonitrile was distilled from P_2O_5 under Ar; and anhydrous LiI was dried at 150 °C in vacuo.

δ-LiV_2O_5. An excess of LiI in acetonitrile solution (25.0 mL, 1.44 M) was added to powdered V_2O_5 (5.005 g, 27.5 mmol), and the resulting mixture was stirred for 24 h at room temperature. The supernatant rapidly developed a dark yellow-brown color characteristic of acetonitrile solutions of I_2. The color of the solid changed from yellow to green to blue-black over several hours. The product was isolated by filtration and washed with acetonitrile. The filtrate and washings were combined, and the I_2 (13.59 mmol) was determined by titration with a standardized aqueous $Na_2S_2O_3$ solution.[14] The indicated stoichiometry was $Li_{0.99}V_2O_5$.

$Li_xV_2O_5$. Compositions of $Li_xV_2O_5$ ($x < 1$) were prepared as above by using the appropriate stoichiometric amount of LiI. The stoichiometry was verified by titration of the I_2 produced. X-ray fluorescence analysis confirmed that no iodine was incorporated by the products.

X-ray powder diffraction data were obtained with a Philips diffractometer using Cu Kα radiation. The magnetic susceptibility data for $Li_xV_2O_5$ were obtained by the Faraday method. Differential scanning calorimetric (DSC) data were obtained with a Du Pont Model 900 thermal analyzer.

Table I. Crystallographic Data for LiV_2O_5

	δ-LiV_2O_5			ε-LiV_2O_5		
hkl	d(obsd), Å	d(calcd),[a] Å	I/I_0	d(obsd),[b] Å	d(calcd),[c] Å	I/I_0
200	5.640	5.636	6	5.698	5.667	15
010	4.970	4.971	100	4.676	4.683	100
110	4.545	4.548	8	4.328	4.328	18
210	3.720	3.728	6	3.614	3.610	10
001	3.392	3.389	10			
101	3.246	3.245	12	3.422	3.422	85
310	2.993	2.997	8	2.945	2.941	40
400	2.818	2.818	8	2.834	2.834	95
111				2.755	2.763	10
301	2.518	2.517	4	2.603	2.602	45
211				2.541	2.545	5
020	2.479	2.485	6	2.328	2.341	15
120				2.289	2.293	35
401	2.164	2.167	4			
411				2.008	2.009	20
320	2.067	2.073	5	1.984	1.990	20
021				1.954	1.961	15
600				1.894	1.889	30
212				1.846	1.853	5
121	1.973	1.973	3			
501	1.875	1.879	7			
511	1.754	1.757	8			
002	1.692	1.694	3	1.787	1.794	30
610				1.755	1.752	20
601				1.669	1.672	15

[a] Calculated values for orthorhombic cell; $a = 11.272$ Å, $b = 4.971$ Å, $c = 3.389$ Å. [b] Pattern taken at 150 °C. [c] Calculated values for orthorhombic cell; $a = 11.335$ Å, $b = 4.683$ Å, $c = 3.589$ Å.

Results and Discussion

A series of bronzes, $Li_xV_2O_5$ ($0 < x \leq 1$), were prepared by the reduction of solid V_2O_5 with lithium iodide in acetonitrile at room temperature according to eq 1. In this reaction

$$V_2O_5 + xLiI \rightarrow Li_xV_2O_5 + (x/2)I_2 \qquad (1)$$

V^{5+} ions within the V_2O_5 lattice are reduced, and Li^+ ions diffuse into the lattice to maintain electroneutrality. This reaction is the reverse of oxidative delithiation with I_2, as observed with $LiVS_2$ (eq 2).[14] The direction of the general

$$LiVS_2 + {}^1/_2I_2 \rightarrow VS_2 + LiI \qquad (2)$$

reaction (eq 3) is determined by the reduction potential of the

$$MY_n + xLiI \rightleftarrows Li_xMY_n + (x/2)I_2 \qquad (3)$$

host lattice. Lithium ions must have a high mobility in the host lattice in order for the reaction to proceed in either direction at an appreciable rate.

The X-ray powder diffraction pattern of LiV_2O_5 (Table I) prepared by the LiI reaction (δ phase) confirms that it is distinct from the γ phase previously reported.[8] A product exhibiting the strongest X-ray diffraction peaks of δ-LiV_2O_5 has been prepared by the lithiation of V_2O_5 with *n*-BuLi.[2] However, we were unable to prepare pure δ-LiV_2O_5 using *n*-BuLi in hexane or other strong reducing agents owing to some unavoidable irreversible overreduction.

A reversible, first-order structural transformation of δ-LiV_2O_5 to a third form (ε-LiV_2O_5) occurs at 125 °C. The enthalpy of this transformation, as determined by DSC, is 1.0 ± 0.1 kcal/mol. An irreversible transformation to γ-LiV_2O_5

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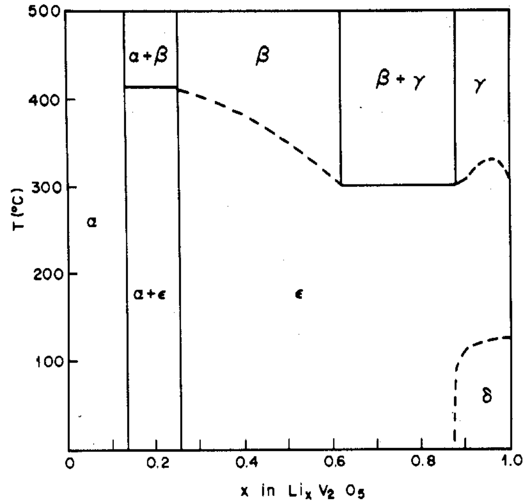

Figure 1. Stability diagram for δ- and ε-$Li_xV_2O_5$.

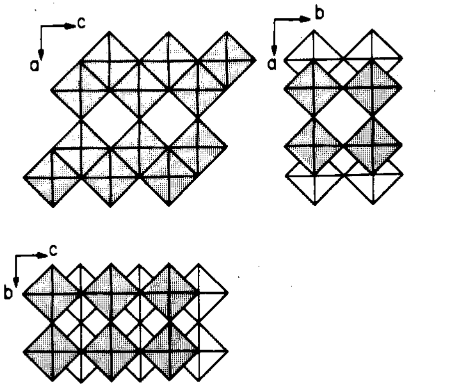

Figure 2. An idealized representation of the structure of V_2O_5 based on octahedral V^{5+} coordination.

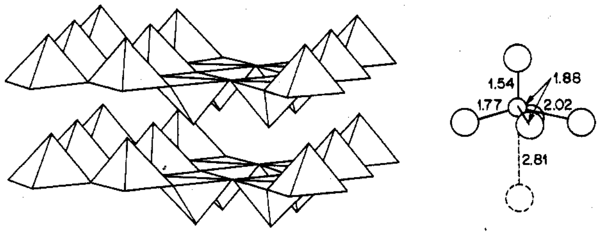

Figure 3. Perspective representation of the V_2O_5 structure assuming square-pyramidal V^{5+} coordination. The V–O bond distances are shown on the right.[15,16]

Table II. V–O Infrared Stretching Frequencies (cm^{-1})[a]

V_2O_5[b]	1020 vs	825 vs, br	...
V_2O_5[c]	1015 vs	830 vs, br	630 s, br
β-$Li_{0.3}V_2O_5$[c]	985 vs, 925 s		
ε-$Li_{0.3}V_2O_5$[c]	1019 vs, 1002 vs, 991 sh	798 s	...
γ-LiV_2O_5[c]	1005 vs, 951 vs, 970 sh	...	564 s, br, 538 sh
δ-LiV_2O_5[c]	1015 vs, 973 sh	...	631 s, br, 528 sh

[a] KBr pressed disks. [b] Reference 17. [c] This work.

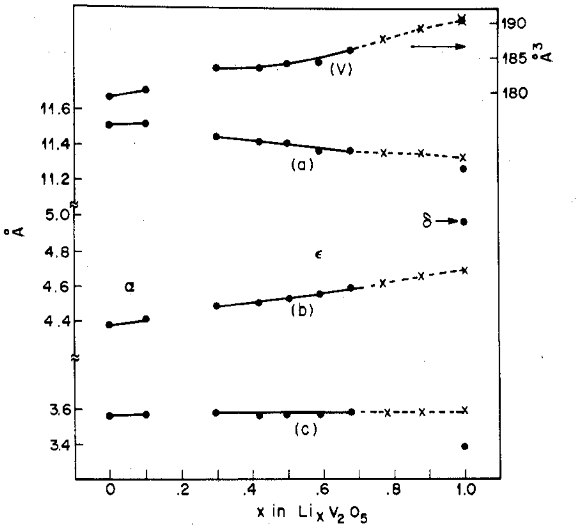

Figure 4. Orthorhombic unit cell parameters of $Li_xV_2O_5$ prepared by the lithium iodide reaction. × denotes data obtained at 150 °C.

(4.0 ± 0.1 kcal/mol) occurs above 300 °C. A stability diagram for the new $Li_xV_2O_5$ phases derived from DSC and X-ray data is shown in Figure 1. The α phase prepared by the lithium iodide reaction is identical with that prepared at high temperature.

The structure of V_2O_5[15,16] is schematically illustrated in Figures 2 and 3. The local geometry of the V^{5+} ions may be viewed as a highly distorted octahedron (Figure 2) with one very short V=O bond (1.54 Å) and one exceptionally long V···O bond (2.81 Å). An alternative description (Figure 3) is based on square-pyramidal coordination of V^{5+} with a weak V···O interaction with a sixth oxygen. The long V···O bonds normal to the *ac* plane allow mica-like cleavage parallel to that plane. The IR transmission spectrum (Table II) of V_2O_5 confirms the presence of vanadyl (V=O) character ($\nu_{V=O}$ = 1015 cm^{-1}). This vanadyl character persists in δ-LiV_2O_5 ($\nu_{V=O}$ = 1015 cm^{-1}), whereas γ-LiV_2O_5 exhibits two distinct peaks at 1005 and 951 cm^{-1}. Similarly, the spectrum of ε-$Li_{0.3}V_2O_5$ exhibits two bands ($\nu_{V=O}$ = 1019 and 1002 cm^{-1}) in the vanadyl region, whereas the absorptions of β-$Li_{0.3}V_2O_5$ occur at lower frequencies than the normal vanadyl range.[17]

A close structural relationship of δ- and ε-LiV_2O_5 to V_2O_5 is suggested by the mild conditions for their formation, the similarity of their IR spectra, and the easy reconversion of these bronzes to V_2O_5 by oxidation with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) in acetonitrile at room temperature. In contrast, γ-LiV_2O_5 is unaffected by DDQ. The orthorhombic unit cell parameters of the α-, δ-, and ε-$Li_xV_2O_5$ bronzes are shown in Figure 4. Within the ε phase, the unit cell parameter *a* gradually decreases, *b* increases, and *c* remains constant. The gradual change of the unit cell parameters of the ε-phase with lithium content from those of V_2O_5 (Figure 4) suggests that the structure of ε-LiV_2O_5 is more closely related to V_2O_5 than is δ-LiV_2O_5. An increase in *b* after lithiation is consistent with the view that lithium incorporation in V_2O_5 occurs with separation of the layers[2] (Figure 2) in a manner analogous to intercalation in van der Waals (vdW) bonded compounds such as MoO_3 and the layered transition metal dichalcogenides. However, we have been unsuccessful in attempts to prepare V_2O_5 bronzes with Na^+ or Me_4N^+ by either reduction with iodide or benzophenone ketyl (for Na) or ion exchange with δ-LiV_2O_5 at room temperature, even though ternary phases of Na and V_2O_5 isostructural with γ-LiV_2O_5 have been prepared at high temperatures.[18] Since vdW bonded compounds generally incorporate these ions readily, we favor the alternative view that interlayer bonding between V_2O_5 layers persists even after lithium incorporation. In addition, if the V_2O_5 layers were separated by the intercalation of Li, then $Li_xV_2O_5$ would be expected to absorb polar solvents such as water or Me_2SO, resulting in increased layer separation as observed for vdW hosts such as Li_xFeOCl,[19] Li_xMS_2,[20] and $Li_{1+x}V_3O_8$.[21] Absorption of water or Me_2SO is not observed for $Li_xV_2O_5$ ($x < 1.0$).

Although the structural data are insufficient at present to determine the nature of the sites occupied by Li^+ ions in the

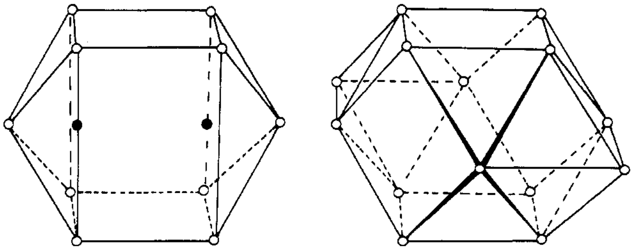

Figure 5. Left: square-pyramidal sites occupied by lithium in β-$Li_{0.3}V_2O_5$;[7] ● = lithium, ○ = oxygen. Right: a cavity containing similar sites present in the V_2O_5 lattice.

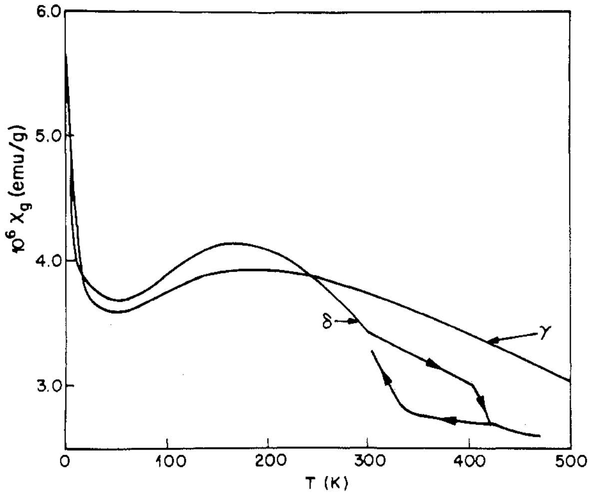

Figure 6. Magnetic susceptibility of δ- and γ-LiV_2O_5.

δ and ε phases, we note that V_2O_5 contains vacant cavities with potential square-pyramidal sites for Li similar to those observed in β-$Li_{0.30}V_2O_5$ (Figure 5).[7]

Treatment of V_2O_5 single crystals with LiI in acetonitrile for several weeks in a sealed tube at 90–100 °C afforded δ-LiV_2O_5 with unchanged overall morphology. However, these crystals easily split into fine filaments parallel to *c*. Weissenberg photographs indicate good crystallinity along *c* but considerable disorder in the other directions. Attempts to measure resistivity of these crystals gave erratic results, but their resistivity at room temperature appears to be of the same order of magnitude as that reported for γ-LiV_2O_5 ($\sim 10^3$ Ω cm).[8]

The magnetic susceptibility data for δ- and γ-LiV_2O_5 are presented in Figure 6. Disregarding the $\delta \leftrightarrow \epsilon$ transformation at about 400 K, we observe the magnitudes and overall shapes of the δ- and γ-LiV_2O_5 susceptibility curves to be quite similar. This suggests that the electronic nature of these phases is also similar. Many vanadium oxides are known to exhibit reversible first-order metal–insulator transitions. In these cases, the metallic phase has a magnetic susceptibility 2–5 times that of the insulating phase.[22] The slight decrease in the susceptibility at the $\delta \rightarrow \epsilon$ transition of LiV_2O_5 (Figure 6) implies that this transition does not arise from a metal–insulator transition. A second transition (probably second order), undetected by X-ray or DSC analysis, is exhibited by δ-LiV_2O_5 at 300 K. The susceptibility of ε-$Li_{0.5}V_2O_5$ is shown in Figure 7. The maximum in the susceptibility curve at about 30 K contrasts with that observed at about 175 K for δ- and γ-LiV_2O_5.

In an attempt to rationalize these magnetic data, the effects of the crystal field strength and spin–orbit coupling on the ordering of the energy levels, the magnetic moment of the V^{4+} (d^1) ion, and the possibility of antiferromagnetic exchange between d^1 centers must be considered. The decrease in the effective magnetic moment with decreasing temperature observed for β-$Li_xV_2O_5$ was accounted for in the following manner.[10] A site symmetry of C_{4v} was assumed for the V^{4+} ion, which results in a splitting of the triply degenerate octahedral field ground state into a doublet and a singlet. The doublet is further split by spin–orbit interactions. The observed data were approximated by assuming that the crystal field splitting was smaller than the spin–orbit splitting and that the ground state was nonmagnetic. However, this approach cannot account for the presence of the low-temperature maximum in the susceptibility of ε-$Li_{0.5}V_2O_5$. The actual site symmetry of the V^{4+} ions is probably much lower than C_{4v}, as is the case for the V^{5+} ions in the parent V_2O_5 structure. A lowering of symmetry is expected to give rise to only orbital singlets with a crystal field splitting several times larger than the spin–orbit coupling. Thus, the ground state is likely magnetic.

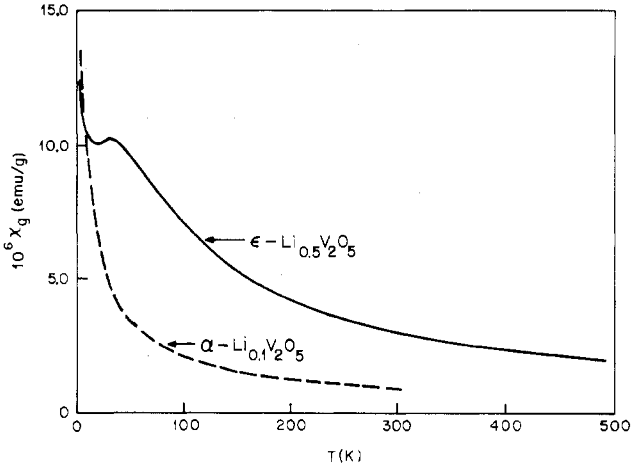

Figure 7. Magnetic susceptibility of ε-$Li_{0.5}V_2O_5$ and α-$Li_{0.1}V_2O_5$.

The presence of a moment on the V^{4+} ions at low temperature implies that the maximum in susceptibility must arise from antiferromagnetic exchange. If this exchange is predominantly one-dimensional, such a maximum is consistent with the Bonner–Fisher theory[23] and no long-range magnetic order will exist at low temperature. If the exchange is two-dimensional, a sharp transition to an ordered magnetic state is not possible since $S = {}^1/_2$.[24] Thus, only a broad maximum in the susceptibility is expected. The temperature of the susceptibility maximum should increase with increasing Li (V^{4+}) concentration since the average number of V^{4+} neighbors would increase. Indeed, for α-$Li_{0.1}V_2O_5$ (Figure 7) no distinct maximum is observed. Further, the fact that the susceptibility continues to rise at low temperatures is inconsistent with a nonmagnetic ground state. Thus, the presence and concentration dependence of the maximum can be best explained by using a model which includes magnetic V^{4+} ions with antiferromagnetic exchange.

Neglecting the contribution to the effective moment resulting from thermal population of crystal field levels above the ground state, we can determine the magnetic moment of V^{4+} by fitting the observed data to the standard Curie–Weiss law (eq 4) with the magnetic moment proportional to $C^{1/2}$.

$$\chi = C/(T + \Theta) + \chi_0 \qquad (4)$$

Magnetic moments of 1.84 μ_B with $\Theta \simeq 60$ K for ε-$Li_{0.5}V_2O_5$ and 1.75 μ_B with $\Theta \simeq 17$ K for α-$Li_{0.1}V_2O_5$ (the spin-only value is 1.73) are calculated. Both curves were fitted for $T \gtrsim 1.3\Theta$. The smaller value of Θ for α-$Li_{0.1}V_2O_5$ may be attributed to the low concentration of spins. However, the continuous increase in the susceptibility of α-$Li_{0.1}V_2O_5$ for 4.2 K < *T* < 20 K implies that some of the V^{4+} ions are isolated and undergo little or no magnetic interaction with other V^{4+} ions, as is expected for dilute moments. Since the data do not extend to temperatures much above the maximum for δ or

γ-LiV_2O_5, the magnetic moments of the V^{4+} ions could not be accurately calculated from eq 4.

Conclusion

The use of LiI in acetonitrile at room temperature as a mild reducing reagent has allowed the preparation and characterization of pure $Li_xV_2O_5$ bronzes distinct from those prepared at high temperatures. These low-temperature phases appear to be structurally more similar to V_2O_5 than are the high-temperature phases. However, the electronic nature of the low-temperature phases appears to be quite similar to that of the high-temperature phases. These studies indicate that V_2O_5 should be regarded as a three-dimensional framework host for lithium rather than a two-dimensional vdW host. This view leads to the conclusion that strengthening the V–O framework should prevent extensive bond breaking under more reducing conditions while still allowing facile lithium incorporation.[25] An example is afforded by $Li_xV_6O_{13}$ bronzes.[3]

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Registry No. LiV_2O_5, 12162-92-4; V_2O_5, 1314-62-1; LiI, 10377-51-2.

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Facile Intramolecular Metalation of Tri-*tert*-butylphosphine in Palladium(II) Hydride Complexes

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Palladium(II) hydrides (*trans*-$PdH(X)(P$-*t*-$Bu_3)_2$ (I) when X = Cl or CF_3COO), prepared by the oxidative addition of HX to bis(tri-*tert*-butylphosphine)palladium(0), have been shown to undergo facile intramolecular metalation in solution producing complexes of the type $PdX(P$-*t*-$Bu_2CMe_2CH_2)(P$-*t*-$Bu_3)$ (II). These complexes (II) when kept in dichloromethane or benzene solution lose 1 molar equiv of phosphine to give the bridged dimeric complexes $[PdX(P$-*t*-$Bu_2CMe_2CH_2)]_2$ (III). Complex III (where X = Cl) is also obtained from the reaction of tri-*tert*-butylphosphine with $PdCl_2(NCPh)_2$ in CH_2Cl_2. Sodium borohydride reduction of complexes I, II, or III in ethanol invariably produces bis(tri-*tert*-butylphosphine)palladium(0). Reaction of *n*-butyllithium with $PdH(X)(P$-*t*-$Bu_3)_2$ in *n*-hexane also gives the palladium(0) complex. The chloride bridge of complex III can be split by a variety of ligands (e.g., pyridine, Ph_3As, Ph_3P, Et_3P, Ph_2MeP, *i*-Pr_3P, *t*-Bu_2MeP, Cy_3P, and $(C_7H_7)_3P$) to give mononuclear species of the type *trans*-$PdCl(P$-*t*-$Bu_2CMe_2CH_2)(L)$.

Introduction

The metalation of bulky phosphines in platinum(II) and palladium(II) dichlorides has been widely studied by Shaw and co-workers.[1,2] It has been suggested that the process is promoted by the facile formation of five-membered rings.[3] Compared with the intramolecular metalation of aromatic carbon atoms in coordinated phosphines, there are only a few examples known for purely aliphatic carbons.[2,4–6] Furthermore, it has been reported[4] that the *n*-propyl groups in the complexes $PtCl_2(P$-*t*-Bu-*n*-$Pr_2)_2$ and $PtCl_2(P$-*t*-Bu_2-*n*-$Pr)_2$ are metalated only when the complexes are heated for several hours, whereas similar palladium complexes cannot be metalated under similar conditions. Although, recently, the intramolecular metalation of *tert*-butylphosphine in the complex $PdCl_2(P$-*t*-$Bu_3)_2$ has been reported,[6] no metalation process has been reported for the corresponding palladium(II) hydrides. Palladium(II) hydride complexes *trans*-$PdH(X)(P$-*t*-$Bu_3)_2$ (where X = Cl or CF_3COO) of sufficient stability to examine metalation processes have recently been prepared by Otsuka et al.[7] We now wish to report that these palladium(II) hydrides undergo rapid intramolecular metalation with the elimination of hydrogen.

Results and Discussion

The preparation of bis(tri-*tert*-butylphosphine)palladium(0) by the reaction of *tert*-Bu_3P with $(\eta^3$-$C_3H_5)Pd(\eta^5$-$C_5H_5)$ has been reported previously.[8] The latter reactant must be obtained from the reaction of thallium cyclopentadienide with allylpalladium chloride, which makes that method time consuming. We have now prepared $(t$-$Bu_3P)_2Pd^0$ in about 70% yield by the reaction of sodium naphthalenide with a mixture of $PdCl_2(NCPh)_2$ or $(COD)PdCl_2$ and P-*t*-Bu_3 in THF. The

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