Vanadium(V) hydrazido(2−) thiolate imine alkoxide complexes†

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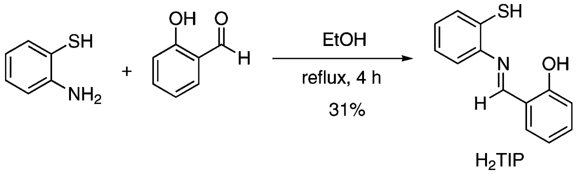
The reaction of $(Me_3Si)_2TIP$ with $V(NNMe_2)(OAr)_3$ results in the production of $V(NNMe_2)(TIP)(OAr)$, where TIP is 2-((2-thiolatophenylimino)methylene)phenolate. The aryloxide is readily displaced by $ISiMe_3$ to form an insoluble iodide complex formulated as $V(NNMe_2)(TIP)(I)$. The iodide was used to prepare three different complexes: $[V(NNMe_2)(TIP)(dmpe)]I$, $[V(NNMe_2)(TIP)(Bu^tbpy)][OTf]$, and $[V(NNMe_2)(TIP)(Bu^tbpy)][SbF_6]$. The phosphine derivative, $[V(NNMe_2)(TIP)(dmpe)]I$, was characterized by X-ray diffraction and shows a quite short N–N distance of 1.293(3) Å indicative of a dominant isodiazene resonance form.

Introduction

Metal hydrazido(2−) complexes are well known intermediates in dinitrogen activation to produce NH_3.[1] Hydrazido(2−) complexes have been synthesized for a large variety of metal centers including Mo, W,[2] Ti, Zr,[3] Re,[4] Os,[5] Pt,[6] Au,[7] Li,[8] U,[9] and Tc.[10] Among these, Mo-based hydrazido complexes have been studied extensively due to their presence in nitrogenase.[11] Similarly, there has been considerable interest in vanadium hydrazido(2−) complexes since the discovery of vanadium in the active sites of similar enzymes.[12,13] The reduction of dinitrogen by these nitrogenase enzymes is believed to involve metal-bound (Fe, Mo, V) hydrazine and hydrazido intermediates.[14] The FeMoco enzyme has been studied extensively and shown by X-ray crystallography to contain a cluster with the Mo atom ligated by one nitrogen, three sulfurs, and two oxygen atoms.[11] It is thought that vanadium in nitrogenase[15] enzymes occupies a similar site. As it is believed that the Mo or V may be the coordinating site for N_2, it is important to understand the hydrazido(2−) chemistry of vanadium with ligands containing S, N, O atoms. In particular, reduction of N_2 to NH_3 by these enzymes might involve intermediate species N_2H_m and NH_n (m = 0–4, n = 0–3) bound at a vanadium site.[14]

In terms of mode of action for vanadium-containing nitrogenase, it has been demonstrated that S_3-ligated vanadium in cluster anions such as $[Fe_3S_4X_3V(DMF)_3]^-$ (X = Cl, Br, or I) binds hydrazines[16] and imides,[17] and catalyzes their reduction.

Vanadium(V) hydrazido(2−) complexes with different ligands (L = S, N, or O) are known in the literature.[18–21] The first example of a vanadium(V) hydrazido(2−) complex with sulfur donor ligands appeared in 1997,[18] $V(NNMe_2)(NS_3)$ where NS_3 = $(SCH_2CH_2)_3N$. This was followed by the synthesis of a series of similar complexes with NS_3^{3-} and OS_2^{2-} ligand backbones on vanadium(V).[19] More recent examples have involved the synthesis of $V(NS_3)(NNC_5H_{10})$ using 1-aminopiperidine to introduce the hydrazido(2−) moiety.[20] In addition, a hydrazido(2−) complex with alkoxide ligands, $Me_2NNV(OAr)_3$, where Ar = O-2,6-$Pr^i_2C_6H_3$, has been reported.[21] However, to the best of our knowledge, no examples of vanadium hydrazido(2−) complexes are known where all of the elemental connections found in the enzyme, S, N, and O, are in the same coordination sphere. As part of our ongoing interest in the study of transition metal hydrazido(2−) complexes,[22] we report the syntheses of vanadium(V) hydrazido(2−) complexes with a chelating ligand containing a thiolate, alkoxide, and donor imine (eqn (1)), 2-((2-thiol-phenylimino)methylene)phenol (H_2TIP).[23]



(1)

Results and discussion

In order to synthesize vanadium(V) hydrazido(2−) complexes with the TIP ancillary, we initially attempted direct reaction of H_2TIP with $V(NNMe_2)(OAr)_3$.[21] However, these reagents did not result in the elimination of 2 HOAr and synthesis of $V(NNMe_2)(OAr)(TIP)$ (**1**) as expected. However, $(Me_3Si)_2TIP$ was synthesized readily and treatment with $V(NNMe_2)(OAr)_3$ produced **1** in good yield (Scheme 1).

In order to explore the chemistry of the $V(NNMe_2)(TIP)$ framework further, we exchanged the aryloxide ligand in **1** with iodide. Treatment of **1** with $ISiMe_3$ in toluene eliminated Me_3SiOAr and produced $V(NNMe_2)(TIP)(I)$ (**2**) in 95% crude yield (eqn (2)). The iodide complex was quite insoluble in most solvents but was effective as a starting material without further purification.

$$\underset{\mathbf{1}}{\mathrm{V(NNMe_2)(OAr)(TIP)}} \xrightarrow[\text{toluene}\atop\text{95\% crude yield}]{\text{1.1 ISiMe}_3} \underset{\mathbf{2}}{\text{"V(NNMe}_2\text{)(I)(TIP)"}} \qquad (2)$$

A brown suspension of iodide **2** in CH_2Cl_2 reacted with dmpe, 1,2-(dimethylphosphino)ethane, to generate a dark red solution (Scheme 2). The new complex, $[V(NNMe_2)(TIP)(dmpe)]I$ (**3**), was isolated in 62% purified yield. Similarly, treatment of **2** with 4,4′-*tert*-butyl-2,2′-bipyridine (Bu^tbpy) and triflate or

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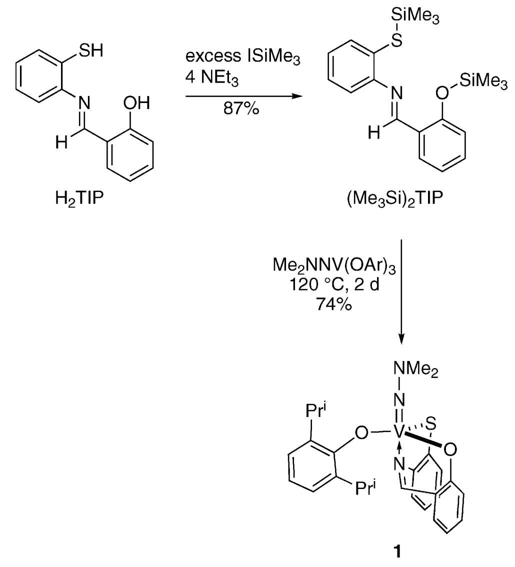
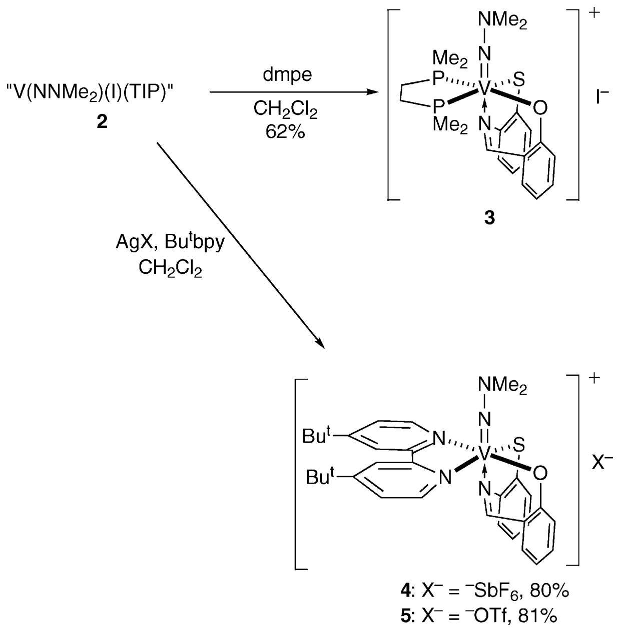


Scheme 1 Synthesis of V(NNMe$_2$)(OAr)(TIP) (**1**).

hexafluoroantimonate silver(I) salts resulted in cationic, hexacoordinate complexes isolable in good yield (Scheme 2).



Scheme 2 Synthesis of cationic hydrazido(2−) complexes.

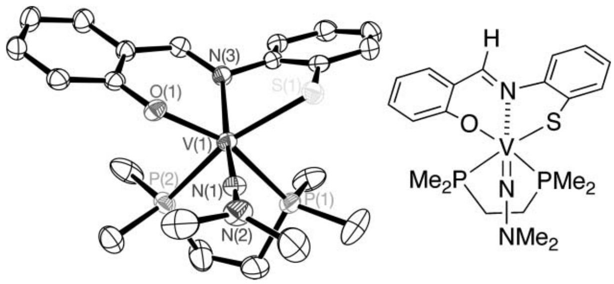


Fig. 1 ORTEP representation of the cation in **3** from X-ray diffraction. Hydrogens and iodide anion are not shown. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): V(1)–N(1) 1.698(2), N(1)–N(2) 1.293(3), V(1)–O(1) 1.908(2), V(1)–N(3) 2.162(2), V(1)–S(1) 2.3383(8), V(1)–P(1) 2.5078(8), V(1)–P(2) 2.5079(8), N(2)–N(1)–V(1) 168.5(2), O(1)–V(1)–S(1) 119.53(6).

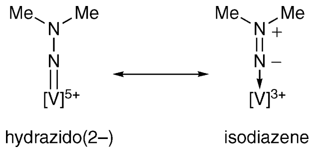


Fig. 2 Hydrazido(2−) *versus* isodiazene resonance forms.

The dmpe complex **3** was characterized by X-ray diffraction, and an ORTEP representation is shown in Fig. 1. Unlike the Ti[22] dimethylhydrazido(2−) complexes reported, this hexacoordinate complex has a planar Me–N–Me moiety, which is common for hydrazido(2−) complexes of most metals.[24] This cationic complex has a short N–N bond of 1.293(3) Å. The shortest hydrazido N–N distances, for example in an iron porphyrin complex,[25] are ~1.23 Å. The hydrazido ligand is similar in metric parameters to a related cationic vanadium complex reported by Dilworth and coworkers.[26] The short N–N bond is indicative of a double bond, and the NNMe$_2$ ligand in this case may be better described as an isodiazene (Fig. 2). While quite different from hydrazido(2−) ligands of Ti in many respects, the short V=N bond, 1.698(2) Å, suggests a significant contribution from the hydrazido(2−) resonance form as well.

Concluding remarks

Using readily prepared V(NNMe$_2$)(OAr)$_3$ as a starting material, an example of a hydrazido(2−) TIP complex, V(NNMe$_2$)(OAr)(TIP) (**1**), can be prepared. Replacement of the OAr ligand with iodide proceeds smoothly with ISiMe$_3$. While this iodide was not fully characterizable due to very low solubility in common solvents, it served as starting material for cationic hydrazido complexes. An X-ray diffraction study on one of the cationic vanadium complexes, [V(NNMe$_2$)(TIP)(dmpe)]I (**3**), revealed a quite short N–N bond. This short N–N bond is indicative of the V(III) cation having poor backbonding into the N=N π* orbital of an isodiazene.

Experimental

General considerations

All manipulations of air sensitive compounds were carried out in an MBraun drybox under a purified nitrogen atmosphere. Pentane (Spectrum Chemical Mfg. Corp.), toluene (Spectrum Chemical Mfg. Corp.), ether (Columbus Chemical Industries Inc.), dichloromethane (EM Science), acetonitrile (Spectrum Chemical), and tetrahydrofuran (JADE Scientific) were sparged with nitrogen to remove oxygen then dried by passing through activated alumina. VCl$_3$(THF)$_3$ was purchased from Strem Chemical Co. and used as received. 1,1-dimethylhydrazine was purchased from Aldrich Chemical Co. and distilled from KOH prior to use. 4,4′-di-*tert*-butyl-2,2′-bipyridine (Bu^{t}bpy) was purchased from Aldrich Chemical Co. and used as received. H$_2$TIP[23] and V(NNMe$_2$)(OAr)$_3$[21] were synthesized according to the literature procedures. Deuterated solvents were dried over purple sodium benzophenone ketyl (C$_6$D$_6$) or phosphoric anhydride (CDCl$_3$)

and distilled under nitrogen. ^{1}H and ^{13}C NMR spectra were recorded on Inova 300 or VXR-500 spectrometers. ^{1}H and ^{13}C NMR spectral assignments were confirmed, when necessary, with the use of 2-D ^{1}H–^{1}H and ^{13}C–^{1}H correlation NMR experiments. Routine coupling constants in ^{13}C NMR spectra are not reported. All spectra were referenced internally to residual protiosolvent (^{1}H) or solvent (^{13}C) resonances. Chemical shifts are quoted in ppm and coupling constants in Hz.

Synthesis of $(Me_3Si)_2$TIP. All the manipulations were carried out inside an inert atmosphere glove box. An Erlenmeyer flask (100 mL) was loaded with H_2TIP (1.00 g, 4.36 mmol) and toluene (1.5 mL). The solution was cooled in a liquid nitrogen cooled cold well inside the box. Triethylamine (1.78 g, 17.6 mmol) in toluene (0.5 mL) was added to the solution. Trimethylsilyl iodide (3.52 g, 17.6 mmol) in toluene (0.5 mL) then was added. After the additions, the reaction was then allowed to warm to room temperature and stir overnight. The reaction mixture became pale yellow with a white precipitate. The precipitate was filtered with a fritted funnel, and the volatiles were removed in vacuo. The product was collected as a viscous, pale yellow oil in 87% yield (1.43 g, 3.9 mmol). ^{1}H NMR (300 MHz, C_6D_6): δ = 7.56 (d, J = 7.48, 1 H, imine-CH), 7.01–6.61 (m, 8 H, aryl), 0.23 (s, 9 H, SiCH_3), 0.15 (s, 9 H, SiCH_3). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ = 150.7, 147.9, 136.1, 128.3, 128.0, 126.2, 124.8, 122.5, 121.4, 120.0, 118.0, 110.7, 64.9, 0.69, 0.23.

Synthesis of V(NNMe$_2$)(TIP)(OAr) (1). Under an atmosphere of dry nitrogen, a threaded pressure tube was loaded with V(NNMe$_2$)(OAr)$_3$ (1.50 g, 2.30 mmol) and (SiMe$_3$)$_2$TIP (0.87 g, 2.30 mmol) in toluene (9 mL). The pressure tube was taken outside the box and heated at 120 °C for 2 d. After cooling the tube to room temperature, the reaction mixture was filtered using a fritted funnel. Volatiles were removed from the brown filtrate in vacuo. This resulted in a dark brown solid. The brown solid was washed with cold pentane, and the residue was dried in vacuo. Finally, the product was crystallized as a dark brown solid from 1:1 ether:pentane in 74% yield (0.87 g, 1.70 mmol). ^{1}H NMR (500 MHz, C_6D_6): δ = 9.21 (s, 1 H, imine-CH), 7.82–6.76 (m, 11 H, aryl-CH), 3.08 (s, 6 H, NCH_3), 2.80 (m, 2 H, CHMe$_2$), 0.84 (d, 6 H, J = 6.9, CHCH_3), 0.81 (d, 6 H, J = 6.9, CHCH_3). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): 167.2, 159.5, 147.8, 145.4, 134.8, 134.3, 134.0, 128.0, 127.2, 124.3, 122.3, 121.6, 120.7, 119.5, 119.4, 116.7, 43.8, 26.2, 22.9, 22.5. ^{51}V NMR (131.6 MHz, CDCl$_3$): 215.2 ($\nu_{1/2}$ = 1813 Hz). Elemental analysis: Exp. (Calc.), C: 63.47 (63.17); H: 6.44 (6.24); N: 8.00 (8.19). M.p.: 152–154 °C.

Synthesis of [V(NNMe$_2$)(TIP)(I) (2). Under an atmosphere of dry nitrogen, a threaded pressure tube (20 mL) was loaded with V(NNMe$_2$)(TIP)(OAr) (0.76 g, 1.50 mmol) and ISiMe$_3$ (0.33 g, 1.70 mmol) in toluene (6 mL). The solution was then heated at 45 °C overnight. A brown precipitate appeared from the reaction mixture. The precipitate was filtered using a fritted funnel. The solid was dried in vacuo. The product was isolated as brown powder in 95% crude yield (0.66 g, 1.40 mmol). Several attempts to purify this compound were unsuccessful as it was highly insoluble, and the compound was used without further purification. M.p.: 216–218 °C.

Synthesis of [V(NNMe$_2$)(TIP)(dmpe)]I (3). Under an atmosphere of dry nitrogen, a vial (20 mL) was loaded with V(NNMe$_2$)(TIP)(I) (0.18 g, 0.39 mmol), and the powder was suspended in CH$_2$Cl$_2$ (1.9 mL). To the stirred suspension was added dmpe (0.058 g, 0.39 mmol). The mixture was stirred overnight. The brown suspension gradually turned into a bright red solution. The volatiles were removed in vacuo. The product was crystallized from 1:1 CH$_2$Cl$_2$:THF in 62% yield (0.15 g, 0.24 mmol). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 9.47 (s, 1 H, imine-CH), 8.19 (s, 1 H, aryl-CH), 7.93 (d, 1 H, J_{HH} = 7.6, aryl-CH), 7.70 (t, 1 H, J_{HH} = 4.5, aryl-CH), 7.65 (t, 1 H, J_{HH} = 7.6, aryl-CH), 7.34 (q, 2 H, J = 2.4 and 3.0, aryl-CH), 7.28 (d, 1 H, J = 8.34, aryl-CH), 7.18 (t, 1 H, J = 6.8, aryl-CH), 3.69 (s, 6 H, NCH_3), 2.11–2.03 (br s, 2 H, CH_2), 1.78–1.75 (dd, 6 H, J = 1.7 and 10.3, PCH_3), 1.78–1.66 (br s, 2 H, CH_2), 0.54–0.37 (dd, 6 H, J = 9.9 and 10.3, PCH_3). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$): 165.6, 164.7, 149.8, 144.1, 144.1, 134.9, 134.7, 129.2, 127.3, 126.1, 121.7, 121.2, 119.2, 44.2, 29.3 (dd, J_{CP} = 12.5 and 27.5 Hz, CH$_2$), 25.2 (dd, J_{CP} = 9.6 and 26.8, CH$_2$), 18.9 (dd, J_{CP} = 3.0 and 27.8, PCH$_3$), 14.6 (dd, J_{CP} = 17.2 and 22.2, PCH$_3$). ^{31}P{^{1}H} NMR (200 MHz): 39.2 (br s). ^{51}V NMR (131.6 MHz, CDCl$_3$):–21.7 ($\nu_{1/2}$ = 1382 Hz). Elemental analysis: Exp. (Calc.), C: 41.11 (41.12); H: 5.15 (5.09); N: 6.77 (6.85). M.p.: 179–181 °C.

Synthesis of [V(NNMe$_2$)(TIP)(Bu^{t}bpy)][SbF$_6$] (4). Under an atmosphere of dry nitrogen, a filter flask (125 mL) was loaded with **2** (0.30 g, 0.65 mmol) and CH$_2$Cl$_2$ (30 mL). The filter flask was cooled inside a liquid nitrogen cooled cold well. Two separate vials (20 mL) were loaded with Bu^{t}bpy (0.17 g, 0.65 mmol) and AgSbF$_6$ (0.21 g, 0.61 mmol). To each reagent vial was added CH$_2$Cl$_2$ (0.5 mL). Both the vials were cooled inside the cold well. The cold solution of Bu^{t}bpy was added to the filter flask. The mixture was allowed to stir for 10 min followed by addition of the AgSbF$_6$ suspension. The reaction mixture then was allowed to warm up to room temperature, sealed, and stirred overnight. The dark brown suspension gradually turned into a reddish-purple solution. The volatiles were removed in vacuo. Then solid products were stirred with THF (25 mL), and AgI separated as a grey solid. The solid was filtered using a fritted funnel. The volatiles were removed *in vacuo* from the filtrate resulting in a reddish-purple solid containing the crude product. The product was crystallized from 1:1 CH$_2$Cl$_2$:pentane in 80% yield (0.34 g, 0.48 mmol). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.82 (d, 1 H, J = 6, bpy-CH), 8.77 (d, 1 H, J = 6, bpy-CH), 8.73 (s, 1 H, imine CH), 7.84–6.83 (m, 12 H, aryl-CH and bpy-CH), 3.76 (s, 6 H, NCH_3), 1.22 (s, 9 H, CCH_3), 1.20 (s, 9 H, CCH_3). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): 166.2, 165.9, 164.7, 163.0, 155.8, 153.2, 152.3, 150.4, 149.1, 147.6, 134.7, 134.1, 127.08, 127.06, 125.7, 122.7, 122.3, 121.7, 121.5, 119.5, 119.1, 118.2, 117.7, 43.6, 35.5, 29.99, 29.92. ^{51}V NMR (131.6 MHz, CDCl$_3$): 423.8 ($\nu_{1/2}$ = 2832 Hz). Elemental analysis: Exp. (Calc.), C: 47.74 (47.16); H: 4.82 (4.68); N: 8.01 (8.33). M.p.: 186–188 °C.

Synthesis of [V(NNMe$_2$)(TIP)(Bu^{t}bpy)][OSO$_2$CF$_3$] (5). Under an atmosphere of dry nitrogen, a filter flask (125 mL) was loaded with **3** (0.30 g, 0.65 mmol) and CH$_2$Cl$_2$ (30 mL). The filter flask was cooled inside a liquid nitrogen cooled cold well. To the suspension was added a cold solution of Bu^{t}bpy (0.17 g, 0.66 mmol) in CH$_2$Cl$_2$ (10 mL) followed by a cold suspension of AgOTf (0.17 g, 0.65 mmol) in CH$_2$Cl$_2$ (5 mL). The reaction mixture was allowed to warm up to room temperature and stir overnight. The brown suspension gradually turned into a dark purple solution. The volatiles were removed *in vacuo* resulting in a dark purple solid. The solid was stirred in THF (25 mL) for 5 h. AgI separated as a grey solid, which was filtered away using a fritted funnel. The volatiles were removed *in vacuo* from the filtrate. The product was crystallized from 1:1 THF:pentane in 81% yield (0.31 g, 0.49 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.87$ (d, 1 H, $J = 8$, bpy-CH), 8.80 (d, 1 H, $J = 8$, bpy-CH), 8.79 (s, 1 H, imine-CH), 7.96–6.84 (m, 12 H, bpy-CH and Ph-CH), 3.75 (s, 6 H, H_3CN), 1.27 (s, 9 H, CCH_3), 1.23 (s, 9 H, CCH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 166.3, 166.0, 164.8, 163.2, 155.9, 153.1, 152.3, 150.6, 149.1, 147.6, 134.6, 134.3, 127.2, 125.6, 122.7, 122.3, 121.5, 119.9, 119.4, 118.4, 117.7, 43.6, 35.6, 30.1, 30.0. ^{19}F NMR (282.4 MHz, $CDCl_3$): $\delta = -79.4$. ^{51}V NMR (131.6 MHz, $CDCl_3$): 423.6 ($v_{1/2} = 2046$ Hz). Elemental analysis: Exp. (Calc.), C: 54.43 (54.18); H: 5.07 (5.22); N: 9.18 (9.29). M.p.: 178–180 °C.

Crystal structure determination of [V(NNMe$_2$)(TIP)(dmpe)]I (3). A red needle crystal with dimensions 0.28 × 0.12 × 0.10 mm was mounted on a Nylon loop using paratone oil. Data were collected using a Bruker CCD diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 173 K. Data were measured using ω and ϕ scans of 0.5°/frame for 10 s. The total number of images was based on results from the program COSMO[27] where redundancy was expected to be 4.0 and completeness of 100% out to 0.83 Å. Cell parameters were retrieved using APEX II software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software. Scaling and absorption corrections were applied using SADABS multi-scan technique supplied by George Sheldrick. The structure was solved by the direct method using the SHELXS-97 program and refined by the least squares method on F^2, SHELXL-97, incorporated in SHELXTL-PC V 6.10. The structure was solved in the space group Pbca. All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. Crystal data: $C_{21}H_{31}IN_3OP_2SV$, $M = 613.33$, orthorhombic, $a = 10.8685(2)$ Å, $b = 18.3385(3)$ Å, $c = 26.2108(5)$ Å, $U = 5224.13(16)$ Å^3, space group *Pbca*, $Z = 8$, 67170 reflections were collected, 6199 were unique ($R_{int} = 0.0556$) which were all used in calculations. The final $R_1 = 0.0566$ and $wR(F_2) = 0.0701$ for all data. The final $R_1 = 0.0325$ and $wR(F_2) = 0.0627$ for all data $I > 2\sigma(I)$.

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