Stepwise insertion of isocyanides and carbon dioxide into vanadium-aryl bonds: chemistry of a tris(.eta.2-iminoacyl)vanadium(III) complex

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configuration. The middle four-membered Re_2S_2 ring is planar (nonbonding S···S = 3.100 Å; S–Re–S = 73.7 (3)°), but the external five-membered ReS_4 rings adopt an envelope configuration, with the S(3) (and S(3a)) atoms occupying the flap positions. Significant alternation of S–S bond lengths, which has been attributed to M–S π-overlap,[12a,e] is not found (S(internal)–S(internal) = 2.011 (13) Å; average S(external)–S(internal) = 2.093 (11) Å).

The nature of the products is highly sensitive to the stoichiometry of the reactants. With a deficiency of sulfur, viz. 2–8-fold molar excess of Re to S_8, a complex mixture of products is formed, from which the title complex is isolated only in trace quantity. When a 1.5-mol excess of sulfur (S_8) is used, the title dimer is formed as a major product. It is tempting to postulate a reaction intermediate such as $[Re(CO)_4(\eta^2\text{-}S_4)]^-$ that can readily undergo decarbonylation and fusion of the metallasulfur rings to form the isolated dimer. Alternatively, one can suggest the dinuclear doubly sulfide-bridged precursor $[(\eta^2\text{-}S_3)(OC)_3Re(\mu\text{-}S_2)Re(CO)_3(\eta^2\text{-}S_3)]^{2-}$, which may easily release the strain of seven-coordination by coupling between the terminal polysulfide chelates and the sulfide bridges, thus forming an extra S–S bond at the expense of a Re–S bond. Such an intermediate would involve a four-membered ReS_3 ring, which is hitherto unknown. Interestingly, a recent report on $[Au_2(\eta^2\text{-}Se_5)_2(\mu\text{-}Se)_2]^{2-}$ [14] has postulated a similar mechanistic pathway, but this mechanism requires a reverse flow of electrons.

The present synthetic route seems to provide the potential for a facile entry into chalcogen-rich complexes.[15] Preliminary results in our laboratory show that $Re(CO)_5^-$ and other carbonylmetalates react readily with selenium and white phosphorus. After this paper had been accepted, we became aware of a report on the selenium compound $[(OC)_3Re(\eta^2\text{-}Se_4)]_2^{2-}$,[17] which has been obtained by another route from Se_4^{2-} and $Re_2(CO)_{10}$ and which shows practically the same structure as the analogous sulfur complex.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles of atoms in the complex (4 pages); a listing of observed and calculated ($10F_o/10F_c$) structure factors (15 pages). Ordering information is given on any current masthead page.

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Stepwise Insertion of Isocyanides and Carbon Dioxide into Vanadium–Aryl Bonds: Chemistry of a Tris(η^2-iminoacyl)vanadium(III) Complex

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Summary: *tert*-Butyl isocyanide inserts in the three V–C bonds of $[V(Mes)_3(THF)]$ (**1**; Mes ≡ 2,4,6-$Me_3C_6H_2$), leading to the tris(η^2-iminoacyl) complex $[V(\eta^2\text{-}Bu^tNCMes)_3]$ (**2**), the structure of which has been confirmed by X-ray analysis and chemical degradation. Complex **2** inserts carbon dioxide into two V–C bonds, forming $[V(\eta^2\text{-}Bu^tNCMes)\{\eta^2\text{-}Bu^tNC(Mes)C(O)O\}_2]$ (**6**). The two metallacycles in complex **6** contain the deprotonated form of an α-imino carboxylic acid.

The multiple insertion of carbon monoxide or isocyanides into an homoleptic metal–alkyl or metal–aryl bond is quite a rare event, as is the migration of an acyl or an iminoacyl group.[1] The latter reaction is the basis for a significant functionalization of organic residues bonded to metal centers.[1] Studying the chemistry of $[(THF)V(Mes_3)]$ (**1**; Mes ≡ 2,4,6-$Me_3C_6H_2$),[2] we observed both a multiple insertion of isocyanides and the migratory capability of an η^2-iminoacyl functionality. Reaction of **1** with Bu^tNC gave at room temperature the insertion of the isocyanide in all three vanadium–aryl bonds, leading to the tris(η^2-iminoacyl) complex **2**.

The analogous reaction with carbon monoxide carried out at −50 °C gave in good yield dimesityl ketone[4] and a, so far, not well characterized vanadium-carbonyl derivative. Dimesityl ketone is derived from a rather rare double

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(3) To a THF (200 mL) solution of 1 (5.62 g, 11.72 mmol) was added dropwise Bu^tNC (2.93 g, 35.30 mmol). The mixture was kept stirring at room temperature for 5 h, and the color changed to dark green. Then the solvent was evaporated to dryness and the residue washed with hexane (40 mL). The solid was recrystallized from hexane (200 mL) (66%). Anal. Calcd for $C_{42}H_{60}N_3V$: C, 76.70; H, 9.12; N, 6.38. Found: C, 76.56; H, 9.02; N, 6.41. μ_{eff} = 2.75 μ_B at 288 K.

(4) Satisfactory NMR, IR, and mass spectra and microanalyses were obtained.

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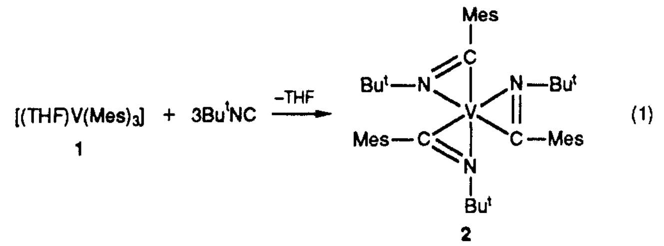
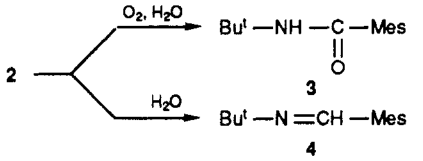


(1)

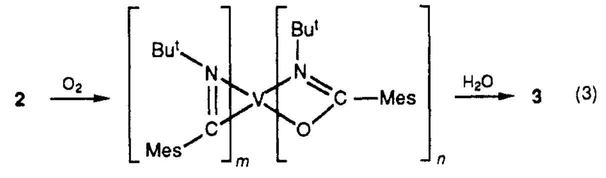
migration of an aryl group to carbon monoxide.[5]

When exposed to the air, complex 2 gave almost quantitatively the amide 3,[4] while hydrolysis produced 4.[4]



(2)

The reaction occurring in the air is quite clearly a two-step reaction:



5 (n + m = 3) (3)

A compound such as 5 should form from 1 and alkyl or aryl isocyanates, as we proved when 1 reacted with $C_6H_{11}NCO$, giving $[V\{C_6H_{11}N{=}C(Mes)O\}_3]$,[6] which was hydrolyzed to the corresponding amide.[4] A picture of 2[7] is given in Figure 1 with some bond distances and angles. All three of the iminoacyl groups are η^2-bonded, giving a formally six-coordinated vanadium complex. However, the structure can also be considered as pseudo trigonal planar with each of the iminoacyl units occupying a single coordination site. For very bulky ligands the trigonal-planar geometry was observed.[6] Another example of a tris(η^2-iminoacyl) complex[8a] and the insertion of an isocyanide into a metal–aryl bond[8b] have been reported by Rothwell. The V–C and V–N distances are essentially identical, and the C–N distances are consistent with a C=N double bond (see caption for Figure 1). The V–C bond distances are close to those of other V–C(sp^2)distances known.[2,9] Such structural data imply a slight contribution to an aminocarbene resonance form for such η^2-iminoacyls.[8] The chemistry of 2 is essentially in agreement with the presence of a V–C σ bond, at least for the reactions studied so far. It has to be emphasized that the insertion of organic functionalities into metal–acyl and –iminoacyl bonds has been so far only episodically and very limitedly observed.[1]

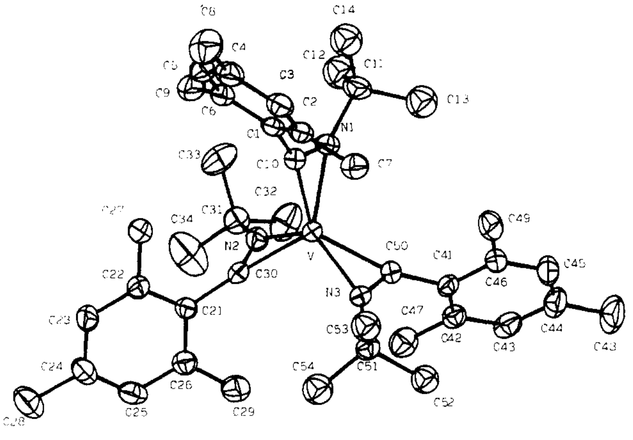


Figure 1. ORTEP drawing of complex 2 showing the atom-labeling scheme (30% probability ellipsoids). Selective bond distances (Å) and angles (deg) include the following: V–N1 = 2.073 (4), V–C10 = 2.072 (6), V–N2 = 2.032 (5), V–C30 = 2.090 (5), V–N3 = 2.099 (4), V–C50 = 2.082 (5), N1–C10 = 1.251 (8), N2–C30 = 1.281 (8), N3–C50 = 1.268 (7), N1–C11 = 1.517 (8), N2–C31 = 1.483 (8), N3–C51 = 1.500 (7); N3–V–C50 = 36.0 (2), N2–V–C30 = 36.2 (2), N1–V–C10 = 35.1 (2).

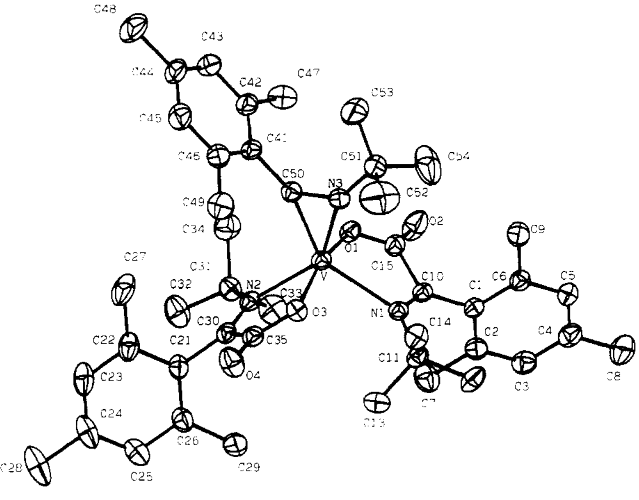
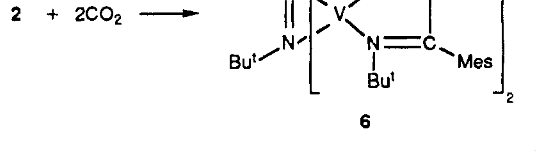


Figure 2. ORTEP drawing of complex 6 showing the atom-labeling scheme (30% probability ellipsoides). Selected bond distances (Å) and angles (deg) include the following: V–O1 = 1.954 (3), V–N1 = 2.352 (4), V–O3 = 1.944 (3), V–N2 = 2.270 (3), V–N3 = 2.004 (3), V–C50 = 2.029 (5), O1–C15 = 1.284 (6), O2–C15 = 1.218 (6), O3–C35 = 1.275 (5), O4–C35 = 1.217 (6), N1–C10 = 1.281 (6), N2–C30 = 1.288 (6), N3–C50 = 1.275 (5), N(1)–C(11) = 1.515 (6), N2–C(31) = 1.511 (6), N(3)–C(51) = 1.494 (5); N3–V–C50 = 36.8 (2), O1–V–N1 = 74.4 (1), O3–V–N2 = 76.4 (1).

We found that 2 reacts with a significant number of inserting groups. This is exemplified by its reaction with CO_2 and $C_6H_{11}NCO$:



6 (4)

Carbon dioxide inserts in two iminoacyl groups, while the more crowded $C_6H_{11}NCO$ gave a monoinsertion product, $[V(Bu^tNCMes)_2\{Bu^tNC(Mes)C(O)NC_6H_{11}\}]$ (7)[6].

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[7] Crystals of 2 are triclinic, space group $P\bar{1}$, with a = 17.913 (2) Å, b = 13.697 (2) Å, c = 8.273 (1) Å, α = 80.40 (1)°, β = 80.30 (1)°, γ = 88.34 (1)°, V = 1972.8 (4) Å^3, Z = 2, and d_{calcd} = 1.108 g/cm^3. The 3758 unique observed data ($I > 2\sigma(I)$) were collected with the use of the $\omega/2\theta$ scanning technique and graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The structure was solved by the heavy-atom method (Patterson and Fourier synthesis) and refined by full-matrix least squares anisotropically, except for the disordered carbon atoms of two butyl groups. The hydrogen atoms, partly located in a difference Fourier map and partly geometrically calculated, were introduced as fixed contributors in the final stage of refinement.

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The nature of 6 and 7 has been established by an X-ray analysis.[6] Some details are reported for 6,[10] shown in Figure 2 with some relevant bond distances and angles.[11] The iminoacyl group does not change its structural parameters. The bonding scheme shown for the two metallacycles derived from the insertion of CO_2 into the V–C carbon bonds is supported by the structural parameters. The bidentate ligand in the metallacycle is the deprotonated form of an α-imino carboxylic acid. The appropriate sequence in the insertion reaction transformed the original aryl group into a doubly functionalized fragment. Insertion of carbon dioxide in a functionalized carbon ligand has so far been an unknown process.[12] Studies will continue for a complete definition of the chemistry of 2, which is a rather unique iminoacyl derivative that does not have at the metal any ancillary ligand.

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Registry No. 1, 79738-18-4; 2, 127973-44-8; 3, 63064-23-3; 4, 127973-43-7; 6, 127973-45-9; 7, 127973-46-0; Bu^{t}NC, 7188-38-7; $C_6H_{11}NCO$, 3173-53-3.

Supplementary Material Available: Tables of crystal data, data collection, and solution and refinement parameters, atomic coordinates, bond distances and angles, thermal parameters, and hydrogen atomic coordinates for compounds 2 and 6 (12 pages); tables of observed and calculated structure factors for compounds 2 and 6 (23 pages). Ordering information is given on any current masthead page.

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[10] A THF (80 mL) solution of 2 (3.33 g, 5.06 mmol) was reacted with CO_2 at room temperature. The color suddenly changed to dark red. The solution was kept stirring for 30 min; then the solvent was evaporated to dryness. A dark solid was obtained, which, after extraction with diethyl ether, gave dark red crystals of 6 (40%). Anal. Calcd for $C_{44}H_{60}N_3O_4V$: C, 70.79; H, 8.04; N, 5.63. Found: C, 70.61; H, 7.97; N, 5.54. $\mu_{eff} = 2.87$ μ_B at 288 K.

[11] Crystals of 6 are triclinic, space group $P\bar{1}$, with $a = 11.253$ (1) Å, $b = 22.818$ (2) Å, $c = 8.538$ (1) Å, $\alpha = 93.85$ (1)°, $\beta = 94.58$ (1)°, $\gamma = 100.95$ (1)°, $V = 2137.9$ (4) Å^3, $Z = 2$, and $d_{calcd} = 1.159$ g/cm^3. The 4002 unique observed data ($I > 2\sigma(I)$) were collected with the use of the $\omega/2\theta$ scanning technique and nickel-filtered Cu Kα radiation ($\lambda = 1.54178$ Å). The structure was solved as above and refined by full-matrix least squares anisotropically for all the non-hydrogen atoms. All the hydrogen atoms were located in a difference Fourier map and introduced as fixed contributors in the final stage of refinement. During the refinement the benzene rings were considered as regular hexagons.

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Stereochemical Aspects of the Reactions of CpMo(CO)$_2$(*syn*-η^3-$C_3H_4COCH_3$)

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Summary: Reduction of CpMo(CO)$_2$(*syn*-η^3-$\underline{CH_2CHCH}COCH_3$) (1) with $NaBH_4$ in MeOH produces (*RR*-(*SS*))-CpMo(CO)$_2$(*syn*-C^3-$\underline{CH_2CHCH}CH(OH)CH_3$) (2) with high diastereoselectivity. Treatment of the latter with 1 equiv of $(CF_3SO_2)_2O$ in ether at −45 °C stereospecifically generates the *s-trans*-η^4-*cis*-pentadiene cationic complex 3, which adds nucleophiles regioselectively and stereospecifically at the α- or δ-carbons. The enolate of 1 generated with lithium diisopropylamide in THF undergoes diastereoselective aldol reactions.

Functionalization of CpMo(CO)$_2$(allyl) complexes in cyclic systems[1-3] has recently attracted considerable attention. Organic functional groups adjacent to the CpMo(CO)$_2$(η^3-allyl) unit can be transformed with excellent stereoselectivity and regioselectivity. In contrast, little has been reported concerning the acyclic allyl system. Faller et al.[4] have reported that condensation of CpMo(NO)(Cl)(*syn*-η^3-crotyl) with aldehydes yields the homoallylic alcohol with high regioselectivity and diastereoselectivity. Stereocontrolled functionalization of acyclic CpMo(CO)$_2$(η^3-allyl) systems represents a significant extension of this chemistry, and we report here stereochemical aspects of the reaction chemistry of CpMo(CO)$_2$(*syn*-η^3-$C_3H_4COCH_3$).

The complex CpMo(CO)$_2$(*syn*-η^3-$C_3H_4COCH_3$) (1) was conveniently synthesized by reaction of CpMo(CO)$_3$Na with 5-chloro-3-penten-2-one (tetrahydrofuran at 0 °C) followed by decarbonylation with excess Me_3NO. The syn and anti isomers of 1, formed in a ratio of 6:1, are readily separable by silica gel column chromatography. For the syn-η^3 isomer, the exo/endo ratio is 16:1. The presence of exo/endo isomers does not complicate the diastereoselectivity studies, because they are related to each other as conformers.[5] Reduction of the syn-η^3 isomer of 1 with $NaBH_4$ in CH_3OH produces (*RR*(*SS*))-CpMo(CO)$_2$(η^3-*syn*-$C_3H_4CH(OH)CH_3$) (2) in an exo/endo ratio of 2:1. The *RR*(*SS*) configuration is assigned to 2 by assuming that hydride adds to the carbonyl group trans to the CpMo-

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