Synthesis and Structure of Dicarbonyl(η³-indenyl)(η⁵-indenyl)vanadium(II). An Unusual Slipped Ring in a Metal Radical

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Although η³-complexes of cyclopentadienyl (Cp), indenyl (Ind), and related ligands are postulated as intermediates in thermal[2] and photochemical[3] reactions, the structurally characterized examples are limited to (η³-fluorenyl)(η⁵-fluorenyl)ZrCl₂,[4] (η³-Ind)(η⁵-Ind)W(CO)₂,[5] (η³-Cp)(η⁵-Cp)W(CO)₂,[6] and (η³-Ind)Ir-(PMe₂Ph)₃.[7] An η³-phenalenyl complex of Pd has been characterized recently by NMR methods.[8] Casey and O'Connor[9] described the formation of (η¹-Ind)Re(CO)₃(PMe₃)₂ from (η⁵-Ind)Re(CO)₃; however, an η³-Ind intermediate was not observed. None of these systems contain a first-row transition metal or are odd-electron species.

Recently we found[10] that CO substitution in (η-C₅Me₅)₂V(CO) obeys a second-order rate law. The mechanism for the bimolecular reaction may involve a 19-electron complex (as postulated[11] for substitution reactions of other metal radicals), an 18-electron complex with the unpaired electron localized on the carbocycle[12] ligand, or a 17-electron complex containing an η³-C₅Me₅ group, as postulated[2] for substitution reactions of 18-electron complexes that contain cyclopentadienyl ligands. Since the η⁵ → η³ → η⁵ mechanism would be expected to show rate enhancement via the
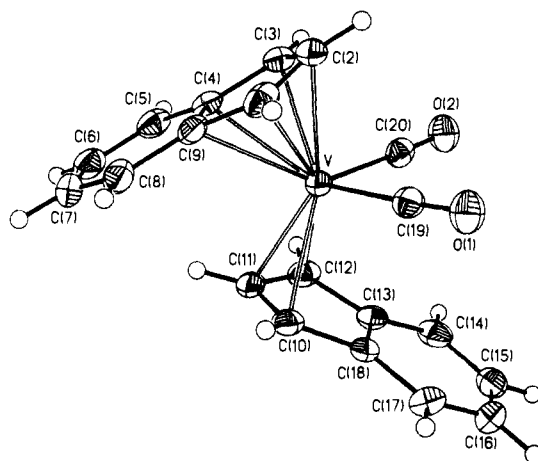

Figure 1. Thermal ellipsoid diagram and labeling scheme (note: C(1), adjacent to C(2), is not labeled because of a lack of space) for dicarbonyl(η³-indenyl)(η⁵-indenyl)vanadium(II).

indenyl effect,[2c-e] we investigated the reaction between (η⁵-Ind)₂V[13] and carbon monoxide. The η⁵-Cp and η⁵-C₅Me₅ analogues are known[14,15] to form stable monocarbonyl adducts. Exposing a hexane solution of (η⁵-Ind)₂V to 1 atm of CO led to the immediate appearance of two absorptions at 1978 and 1926 cm⁻¹ in the IR spectrum. This suggested formation of a dicarbonyl complex (η³-Ind)(η⁵-Ind)V(CO)₂ (A), similar to the 18-electron tungsten analogue.[5] No absorption was detected in the region expected for a monocarbonyl adduct (e.g., (η⁵-Cp)₂VCO absorbs[15] at 1881 cm⁻¹). The solution EPR spectrum showed an eight-line signal from vanadium hyperfine splitting (g_{iso} = 1.9835, A_{iso} = 47 G) that is typical of 17-electron vanadium complexes. This suggests that the unpaired electron is not localized on the carbocycle ligand. Solutions of the dicarbonyl complex are sensitive to air and heating; they revert to the parent metallocene in vacuo. On warming these solutions under a CO atmosphere, an idenyl ligand was lost to form the known species[16] (η⁵-Ind)V(CO)₄.

By cooling a hexane solution of A, dark green crystals were obtained in 70% yield whose crystal and molecular structure (Figure 1) were determined[17] by X-ray diffraction. The structure shows pseudooctahedral coordination geometry about vanadium with OC–V–CO∠ = 85.8 (1)° and both C–O = 1.145 (4) Å. The η³-Ind group contains three short V–C bonds (V–C(10) = 2.379 (3) Å, V–C(11) = 2.184 (3) Å, V–C(12) 2.359 (3) Å) and two nonbonding or weakly bonding V–C distances (V–C(13) = 2.857 (3) Å and V–C(18) = 2.876 (3) Å). The C–C bond distances in the five-membered ring show evidence of an allyl-ene distortion: C(10)–C(11) = 1.403 (6) Å; C(11)–C(12) = 1.404 (6) Å; C-(12)–C(13) = 1.457 (5) Å; C(10)–C(18) = 1.453 (4) Å; C-(13)–C(18) = 1.415 (5) Å. For the η⁵-Ind ring there is a slight slippage[18,19] toward the η³-structure: V–C(1) = 2.261 (3) Å,

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(13) The (η⁵-Ind)₂V was synthesized in 20-30% yield following the procedure[14] used to prepare (η-C₅Me₅)₂V. Anal. Calcd for C₁₈H₁₄V: C, 76.87; H, 5.01. Found: C, 75.35; H, 5.10. Mass spectrum (70 eV): parent ion *m/e* 281.

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(17) VC₂₀H₁₄O₂: monoclinic, *P*2₁/*n*, *a* = 6.609 (1) Å, *b* = 23.843 (4) Å, *c* = 10.166 (1) Å, *β* = 105.98 (1)°, *V* = 1540.0 (4) Å³, *Z* = 4, *D*(calcd) = 1.45 g cm⁻³, μ = 6.7 cm⁻¹ (Mo Kα), 23 °C. Green-black needle, 0.10 × 0.18 × 0.51 mm, Nicolet R3 diffractometer, 4° ≥ 2θ ≥ 48°, ω scans 5-20°/min, <1% decay, 2654 data collected, 2426 unique and 1861 observed (F_o ≥ 4σ(F_o)). Heavy-atom solution, blocked cascade refinement, all non-hydrogen atoms anisotropic, all hydrogen atoms as idealized, isotropic contributions. R_F = 0.039, R_{wF} = 0.042 based on the 1861 reflections, GOF = 1.15, Δ/σ(last cycle) = 0.004, highest difference map peak = 0.26 e/Å³. SHELXTL computer programs (Nicolet Corp., Madison, W1).

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Table I. Slip Parameters*a* for (η^3-Ind)(η^5-Ind)V(CO)$_2$ (A) and (η^3-Cp)(η^5-Cp)W(CO)$_2$ (B)

complex	$\Delta = |S|$, Å	σ, deg	ψ, deg	ΔM–C
A, η^5-Ind	0.157	0.0	4.6	0.13
η^3-Ind	0.798	1.5	20.9	0.56
B, η^5-Cp	0.076	0.0	2.2	0.10
η^3-Cp	0.928	0.0	23.4	0.62

a Parameters are defined in ref 18 and 19. $|S|$ represents the slippage distance of the ring centroid from the projection of the metal atom on the ring, σ is the angle between the S vector and the vector from ring centroid to the unique "allyl" carbon, ψ is the angle between the normal to the plane and the centroid–metal vector, and ΔM–C is the difference between the average of the metal carbon distances to the "allyl" and "ene" carbons.

V–C(2) = 2.237 (3) Å, V–C(3) = 2.272 (3) Å, while V–C(4) = 2.386 (3) Å and V–C(9) = 2.388 (3) Å. Faller, Crabtree, and Habib[18] have compared slippage parameters for known indenyl and cyclopentadienyl structures. Slip parameters for A and (η^3-Cp)(η^5-Cp)W(CO)$_2$,[18] B, are compared in Table I. Complex A represents a less extreme case than B but shows significantly more slippage than known η^5-systems ($\Delta < 0.3$).[18]

Even though complex A is expected to be more crowded than the isostructural tungsten[5] species, distortion of the η^3-Ind group from planarity is small. The dihedral angle between the η^3-carbons and the remaining carbon atoms of the η^3-Ind group for A is 12.0 (3)° in contrast to that of 26° for[5] (η^3-Ind)(η^5-Ind)W(CO)$_2$ or 28° for[8] (η^3-Ind)Ir(PMe$_2$Ph)$_3$. Similar to these structures, the apex atom, C(11), of the η^3-fragment is 0.2 Å closer to the metal than the remaining carbons. Distances from the η^3-fragment to V(II) in this complex are shorter (by ∼0.08 Å) than in (η^3-Ind)(η^5-In)W(CO)$_2$.[5] Two of the V–C(allyl) distances are equivalent to those in (η^3-Ind)Ir(PMe$_2$Ph)$_3$; however, the apex atom in the Ir system is only 2.047 (8) Å from the metal. The greater planarity of the indenyl ring in A, the reduced value of Δ, and the long, but perhaps weakly interacting V–C(13) and V–C(18), distances suggest that the ene portion of the η^3-ring donates weakly to vanadium thereby reducing the electron deficiency at the 17-electron center. If the unpaired electron is localized toward the ene fragment then a 3-center-3-electron bond may begin to form analogous to the 2-center-3-electron bond postulated[11h] to explain the facile associative substitution pathway in 17-electron carbonyl complexes.

These results provide crystallographic evidence that first-row metals can support the slipped η^3-structure that has previously been structurally characterized for 18-electron complexes of heavier metals. For the first time ring slippage has been shown for a metal radical. These results further suggest that the 17-electron systems Cp$_2$VCO and (η^5-C$_5$Me$_5$)$_2$VCO, which substitute CO by a bimolecular process, may involve a 17-electron transition state or intermediate that contains a slipped ring. The question of whether 19-electron intermediates or 17-electron intermediates containing a slipped η^3-ring (or both) are present in reactions of metal cyclopentadienyl radicals remains to be answered.

Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, anisotropic temperature factors, hydrogen atom coordinates, and calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

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A New Inversion Process at Group V (Group 15)[†] Elements. Edge Inversion Through a Planar T-Shaped Structure

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We report a new mechanism for inversion of tricoordinate pyramidal pnictogens, 8-Pn-3 (Pn = P, As, Sb). Classical inversion of these species is believed to proceed through a trigonal-planar transition state. The recent synthesis[1–3] of molecules containing a planar T-shaped pnictogen (1) suggests that similar geometries could be involved in inversions at some 8-Pn-3 centers.

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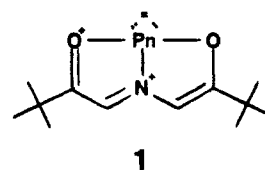
The classical inversion barrier at pyramidal phosphorus is expected to be quite high with electronegative substituents. The inversion barrier in PH$_3$ is calculated as 42.1 kcal/mol with a double-ζ + d(P) basis set, whereas the barrier for PH$_2$F is calculated as 62.1 kcal/mol.[4a] Calculations on planar D_{3h} PF$_3$ reveal that the lone pair is not in a 3p orbital (a_2'') but rather is in an a_1' orbital with a 3s component.[4b,5] On the basis of ab initio calculations described below, we propose that with appropriate electronegative substituents, the pyramidal phosphorus species (and by analogy heavier pnictogens) will invert through an approximate T-shaped transition state (or intermediate).

Calculations were performed at the SCF level[6] with a polarized double-ζ basis set.[7] All geometries were gradient-optimized in the appropriate symmetry.

Calculations were done for the successive fluorination of phosphine: PH$_3$, PH$_2$F, PHF$_2$, PF$_3$. The optimum geometries for the pyramidal (A), planar "D_{3h}" (B), and planar "T-shaped" (C) structures are given in Table I. Our calculated structures are in good agreement with the experimental geometries for pyramidal PH$_3$, PHF$_2$, and PF$_3$.[8–10] Good agreement for the py-

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