A second thermodynamic cycle (Scheme II), which requires thermodynamic data for hydrogenation of the aromatic compound (eq 6) and the pK_a of the dihydroaromatic (eq 7) in addition to the electrode potential data (eq 8 and 9) results in an expression (eq 12) to estimate the pK_a of the conjugate acid of the anion radical, i.e., $pK(AR)$.

The direct determination of $pK(DA) - pK(AR)$ from a single cyclic voltammogram (Scheme I) is illustrated in Figure 1. The reversible couple, R_1/O_1, corresponds to electrode reaction 8 where A represents anthracene. The reversible reduction of the anion radical to the dianion (eq 1) takes place at R_2.[8] On the return scan the process at O_2 involves the oxidation of AH^- (eq 2). The reversible potential estimated for reaction 2 is in error by the kinetic shift due to the irreversible reaction of $AH\cdot$. The magnitude of the error can be estimated by using well-known theoretical relationships.[10]

The data in Table I illustrate the determination of $pK(AR)$ for the conjugate acid of the anthracene anion radical in DMSO making use of Scheme II and literature data for equilibria 6 and 7. The value obtained, $pK(AR) = 23$, indicates that the anion radical is significantly less basic than AH^-, the monoanion of 9,10-dihydroanthracene ($pK(AH_2) = 27$). Electrode potential data taken from Figure 1 indicate that $pK(DA) - pK(AR)$ (Scheme I) is equal to 30 which results in a value of 53 for $pK(AH^-)$. These values appear to be consistent with previous observations. Reversible cyclic voltammograms for formation of dianions can only be observed when water and other protic impurities are rigorously excluded.[11] On the other hand, reversible formation of anion radicals can be observed even in the presence of significant concentrations of water. The oxidation peak for the carbanion is only observed when the water concentration is quite low.[12] This would appear to be at least qualitatively in line with the pK_a values that we have determined by using the two thermodynamic cycles.

A value of $pK(AH^-)$ has been reported previously by Streitwieser.[13] Only 4 pK units difference were observed for the first and second ionization constants of dihydroanthracene in cyclohexylamine. This was attributed to the relative inherent stability of the dianion derived from delocalization energy and, more importantly, to triple ion formation with two cesium ions. The large discrepancy in this pK_a difference with what we observe could arise from the fact that the dianion is not expected to associate strongly with tetrabutylammonium ions used in this study in DMSO as solvent.

The only source of significant error in our estimate of $pK(DA) - pK(AR)$ derives from equating the potential measured for the oxidation of AH^- to the reversible value. The possibility of a kinetic shift contribution to this potential makes the measured potential difference, $E_2^\circ - E_1^\circ$, a minimum value. Thus our estimate of $pK(DA) - pK(AR)$ is minimal, subject to a possible correction of $+2$ pK_a units. The major assumption in our treatment is the value of the pK_a of AH_2 in DMSO. We estimate that this assumption could give rise to an error as much as 2 pK_a units. Therefore, the value of $pK(DA) - pK(AH_2)$ in DMSO is 27 $\pm$ 3. The value reported for the cyclohexylamine/cesium$^+$ system then differs from ours by about 23 pK_a units. Since ion pair $AH^-(Cs^+)$ and triple ion $A^{2-}(Cs^+)_2$ formation are expected to affect $pK(AH_2)$ and $pK(DA)$ in the same direction, we find a difference of 23 for ΔpK_a, free ions vs complexed ions, somewhat more than expected. The resolution of this problem requires

further work. Our method should be applicable to the cyclohexylamine/cesium$^+$ system and provides a more direct comparison between free and complexes ions.

The two thermodynamic cycles (Schemes I and II) are readily applied to a variety of other anion radicals, dianions, and the corresponding dihydroaromatic compounds. When experimental data for reaction 6 are not available, it may be possible to obtain satisfactory results by using theoretical data from molecular mechanics calculations.[14] The quantity of most interest with regard to the reactivity of anion radicals toward proton donors is $pK(DA) - pK(AR)$ and this can be determined to a high degree of precision by using only electrode potential measurements.

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Transition-Metal Compounds with Bridging Nitride Ligands. Synthesis and Structure of *cis*-(Me₃SiO)₃V≡N—Pt(Me)(PEt₃)₂

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Inorganic and organometallic polymers have recently become the subject of intense interest and study because of their unusual properties[1] and their potential for applications in the areas of electronics[2] and ceramics.[3] In comparison to organic polymers, however, general and versatile methods for the synthesis of inorganic and organometallic polymers are not readily available.[4] In particular, the preparation of polymers which (1) contain transition-metal atoms and (2) have these metal centers incorporated into the polymer backbone has received very little attention.[1,5] This may be, in part, because known reactions that couple two ligated metal centers, by formation of either direct metal–metal bonds or bonds to a bridging ligand, have a strong tendency to produce cluster compounds on addition of subsequent metal centers.[6] We are examining the synthesis of molecules in which two metal centers are linked by a single, bare nitrogen atom, the μ_2-nitride ligand. Our approach utilizes condensation of a trimethylsilylimido complex with a metal halide derivative to

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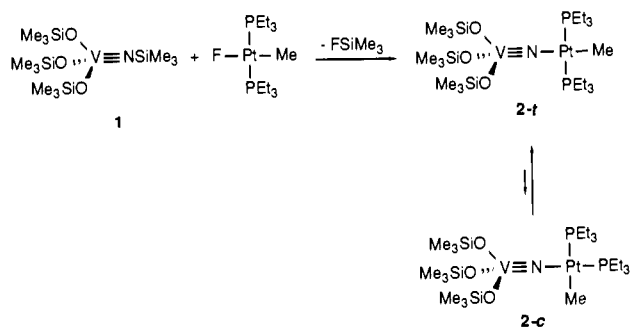(9) Hammerich, O.; Parker, V. D. *Electrochim. Acta* **1973**, *18*, 537.

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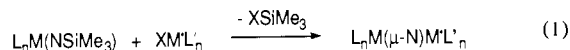(11) Jensen, B. S.; Parker, V. D. *J. Am. Chem. Soc.* **1975**, *97*, 5211.

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Communications to the Editor

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Scheme I

produce a μ_2-nitride complex on loss of trimethylsilyl halide (eq 1). In this report, we describe the synthesis and characterization

$$L_nM(NSiMe_3) + XM'L'_n \xrightarrow{\text{- XSiMe}_3} L_nM(\mu\text{-N})M'L'_n \qquad (1)$$

of two isomers of a novel heterobimetallic complex in which a vanadium and a platinum center are bridged by the nitride ligand. These complexes are models for new polymers based on a metal nitride backbone[7,8] and demonstrate the utility of the synthetic method described in eq 1.

The vanadium(V) trimethylsilylimido complex, $(Me_3SiO)_3V\equiv NSiMe_3$[9] (**1**), reacts immediately and quantitatively (^{1}H NMR) with *trans*-FPt(Me)(PEt_3)_2[10] in benzene solution at 22 °C producing 1 equiv each of fluorotrimethylsilane and *trans*-$(Me_3SiO)_3V\equiv N$—Pt(Me)(PEt_3)_2 (**2-t**)[11] (Scheme I). The ^{1}H NMR spectrum of **2-t** shows methyl and methylene resonances due to the two triethylphosphine ligands characteristic of trans coordination at platinum(II). Compound **2-t** is also formed as the major product (60%) in the reaction of **1** with *trans*-ClPt-(Me)(PEt_3)_2[10b] at 80 °C. Crystallization of **2-t** from pentane affords yellow crystals of an isomer with a ^{1}H NMR spectrum indicating cis coordination of the two PEt_3 ligands at platinum(II), *cis*-$(Me_3SiO)_3V\equiv N$—Pt(Me)(PEt_3)_2 (**2-c**).[11] Lower solubility for the cis isomer is common for square-planar platinum(II) bis(triethylphosphine) complexes.[12] Benzene solutions of **2-c** undergo slow isomerization back to the thermodynamically favored isomer **2-t** (Scheme I).

An X-ray diffraction study of crystalline **2-c** (Figure 1)[13] indicates that the nitride ligand connects a d^0 vanadium(V) center
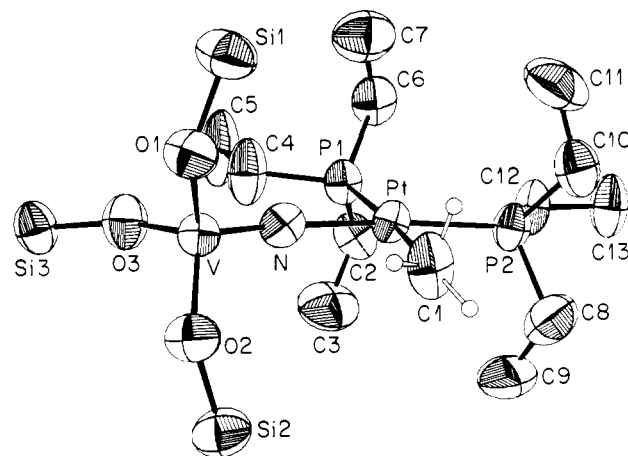

Figure 1. ORTEP drawing of *cis*-$(Me_3SiO)_3V\equiv N$—Pt(Me)(PEt_3)_2 (**2-c**) with 50% probability thermal ellipsoids for non-hydrogen atoms. Methyl carbons on trimethylsiloxide ligands have been omitted for clarity. Selected bond distances (Å) and angles (deg) not mentioned in text: V–O(1), 1.795 (6); V–O(2), 1.794 (6); V–O(3), 1.813 (6); Pt–C(1), 2.112 (10); Pt–P(1), 2.318 (2); Pt–P(2), 2.253 (2); O–V–O, 111.6 (3), 111.5 (3), 110.7 (3); O–V–N, 108.0 (3), 108.7 (3), 106.0 (3); V–O–Si, 139.7 (4), 142.1 (4), 149.3 (4); P(1)–Pt–N, 90.29 (18); P(1)–Pt–P(2), 100.46 (9); P(2)–Pt–C(1), 85.4 (4); N–Pt–C(1), 83.9 (4).

to a d^8 platinum(II) center in a roughly linear asymmetric nitride bridge, V≡N—Pt. The V–N distance of 1.600 (7) Å is typical of vanadium–nitrogen triple bonds.[14] The Pt–N distance of 2.030 (7) Å is consistent with a platinum–nitrogen single bond, significantly shorter than the Pt–N distances (2.15–2.21 Å) found for platinum(II) amine adducts in which the N-donor ligand is trans to a trialkylphosphine ligand.[15] V, Pt, N, P(1), P(2), and C(1) define a plane ±0.02 Å, maintaining the square-planar coordination about the platinum(II) center. The VNPt angle of 168.5 (4)° is somewhat smaller than VNC angles observed for tetrahedral vanadium(V) imido derivatives,[14] probably due to the steric congestion between the adjacent OSiMe_3 and PEt_3 ligands, although contributions from the bent nitride valence tautomer, $(Me_3SiO)_3V=\ddot{N}$—Pt(Me)(PEt_3)_2, to this small deviation from linearity can also be considered.

Compounds **2-t** and **2-c** are unusual in that they possess covalent bonds between the nitride ligand and two very different metal centers, only one of which is involved in π-bonding (A).[16] This

$$M\equiv N — M' \qquad M\equiv N:\!—M'$$

| A | B |

is a direct consequence of the condensation reaction employed. In contrast, other reported asymmetric μ_2-nitride complexes,[17-19] such as $(Et_2PhP)_3Cl_2Re\equiv N:\!\rightarrow PtCl_2(PEt_3)$ (**3**),[17a] are best formulated as adducts involving dative coordination of a terminal

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(13) Crystal data for **2-c**: monoclinic, $P2_1/c$; a = 20.093 (3) Å, b = 10.134 (2) Å, c = 20.187 (3) Å, β = 113.17 (1)°, V = 3779 (2) Å^3, Z = 4, D_{calcd} = 1.027 g cm^{-3}, 25 °C. An Enraf-Nonius CAD4 diffractometer was used to collect 7073 reflections (two octants, $2\theta \leq 50°$). After an empirical absorption correction (μ(Mo K_α) = 43.5 cm^{-1}), the structure was solved by conventional heavy-atom methods using 3518 unique data with $I > 3\sigma(I)$. The three Pt–CH_3 hydrogens were located on a Fourier difference map and positionally refined; 48 H atoms were fixed in calculated positions; nine H atoms on the badly elongated C14, C15, and C16 atoms were not included. Refinement with all 33 non-hydrogen atoms anisotropic yields R = 3.8% and R_w = 4.3%; GOF = 1.28, highest final residual electron density, ±1.2 e/Å^3 near Pt, ±0.6 e/Å^3 elsewhere.

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nitrido ligand to a coordinatively unsaturated metal center (B). The critical difference between these two types of complexes is that the nitride bridges in **2-*t*** and **2-*c*** (A) are more robust than in complexes of type B. For example, whereas **3** dissociates to neutral (Et$_2$PhP)$_3$Cl$_2$Re≡N: and [PtCl$_2$(PEt$_3$)]$_2$ on attempted isolation,[17a] we do not observe dissociation of the μ_2-nitride bridge in **2** to produce an anionic terminal nitrido complex and a cationic metal center. This feature of the condensation reaction may prove important in synthesizing metallonitride polymers.

In summary, we have shown that a simple condensation reaction can be used to form a novel nitride-bridged vanadium–platinum derivative possessing robust metal nitrogen bonds. We are exploring the use of reaction 1 in the synthesis of not only bimetallic μ_2-nitride complexes but also transition-metal-containing nitride polymers.[7]

Supplementary Material Available: Crystallographic data for **2-*c***—ORTEP plot of all non-hydrogen atoms, crystal data, atomic coordinates, bond distances and angles, anisotropic temperature factors, and hydrogen atom coordinates (6 pages); observed and calculated structure factors for **2-*c*** (18 pages). Ordering information is given on any current masthead page.
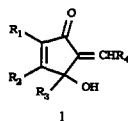
A Stereoselective, Palladium-Catalyzed Route to 4-Oxygenated 5-Alkylidenecyclopentenones and 3-Oxygenated 2-Alkylideneindanones

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Eicosanoid derived marine natural products containing a 4-oxygenated 5-alkylidenecyclopentenone core **1**, such as the cla-

1

vulones[2] (claviridenones[3]) chloro-,[4] bromo-, and iodovulones,[5] and the punaglandins,[6] have been reported to possess remarkable cytotoxicity in both in vitro and in vivo studies.[7] In fact, non-

naturally occurring arylidene cyclopentenediones also show significant in vitro antitumor activity.[8] The synthesis of 4-oxygenated 5-alkylidenecyclopentenones has been explored by numerous workers, although the stereoselectivity of the alkylidene formation has been rarely addressed.[9] We wish to describe a new, highly stereoselective, palladium-catalyzed reaction that provides rapid access to highly functionalized 4-oxygenated 5-alkylidenecyclopentenones and to 3-oxygenated 2-alkylideneindanones. The reaction holds promise for the synthesis of the naturally occurring eicosanoids mentioned above as well as for the synthesis of simpler analogues of the natural products.

Alkynyl anions add in high yield to cyclobutenediones[10] and benzocyclobutenediones[11] to give 4-alkynyl-4-hydroxycyclobutenones and 2-alkynyl-2-hydroxybenzocyclobutenones, respectively, and the reaction occurs with good regioselectivity with a number of unsymmetrically substituted substrates.[12] Excellent literature precedent[13] suggested that the 4-alkynyl-4-hydroxy-

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