Summary and Conclusions

The LEED intensity data reveal that *two* ordered phases are formed on adsorbing $C_4H_4Cl_2$ at both 150 and 300 K. While it is possible that the mixed overlayer involves long-range ordering of both the hydrocarbon species and chlorine, this interpretation is made less likely by the observed temperature dependence. In particular, the structure persists in a temperature regime where extensive hydrocarbon reactions are occurring. Therefore, the simplest interpretation is that the first pattern to appear corresponds to a (2 × 2) chlorine mesh (Cl coverage = 1/4). The second pattern could then be assigned to a (2 × 1) chlorine phase (Cl coverage = 1/2) which is present as three symmetry-related domains. This view is confirmed by recent HREELS measurements.[9] Possible surface structures are indicated in Figure 11, the important point being that completion of the second structure is found to occur just before the coverage at which dissociation of $C_4H_4Cl_2$ is substantially inhibited.

Before proceeding to a consideration of the mechanism of benzene formation, it is worth noting that the present results shed some useful light on the mode of ethene formation in the system. Earlier work has suggested that on Pd(111) vinylidene is the intermediate which is formed from ethyne and which eventually undergoes hydrogenation to ethene.[4] Here, we observe that C_2H_4 is desorbed in a similar fashion when C_4H_4 rather than C_2H_2 is the species initially present on the surface; a possible new route from ethyne to ethene (via C_4H_4) appears to be indicated. However, HREELS data[9] show that C_4H_4 rearranges to vinylidene at a temperature below that at which C_2H_4 desorbs, so that even this pathway involves the formation of a vinylidene intermediate.

The ethene desorption profiles measured for $C_4H_4Cl_2 + C_2D_2$ coadsorption experiments showed an interesting coverage dependence when $C_4H_4Cl_2$ was adsorbed at 300 K; only a small amount of ethene desorbs below 300 K for $C_4H_4Cl_2$ exposures <70 s, but above this exposure the yield of desorbing ethene rapidly increases and the C_2H_4 peaks shifts to 350 K. The hydrogen species desorption profile also changes markedly between these two cases; the sharp leading edge of the low $C_4H_4Cl_2$ exposure experiments at 450 K is removed and a much flatter desorption profile is observed.

We postulate that the switch in behavior is due to the formation of ethylidyne rather than vinylidene from C_4H_4 when the surface coverage is low. This conclusion is supported by HREELS measurements on the decomposition of C_4H_4.[9]

A principal object of this work was better understanding of the mechanism of ethyne cyclotrimerization on Pd(111), and evidence has been presented that $C_4H_4Cl_2$ acts as a reagent for depositing C_4H_4(a) species on the surface. The results of the $C_4H_4Cl_2$ + C_2D_2 experiments establish that the C_4H_4 moiety is built directly into the product benzene as C_4H_4 rather than $2C_2H_2$; this is demonstrated by the observed isotopic distribution. Futhermore, the C_6D_6 "by-product" which is formed in these experiments shows a MTPR profile which exactly mirrors that of the $C_6H_4D_2$. This demonstrates that the two kinds of benzene are formed by routes which are very closely related; indeed they are energetically indistinguishable in these experiments:

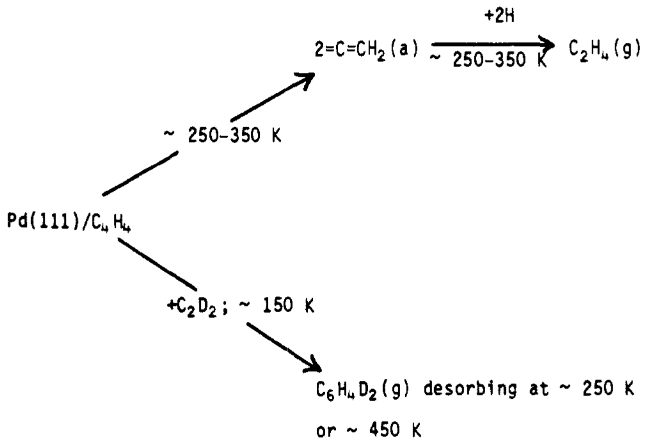
$$3C_2D_2(a) \rightarrow C_6D_6$$

and

$$C_4H_4(a) + C_2D_2(a) \rightarrow C_6H_4D$$

appear to be equivalent pathways. Control experiments show that the high-temperature benzene peak is associated with molecules which are chemisorbed in the same state as those resulting from the direct adsorption of benzene, i.e., "flat-lying". The low-temperature peak is accordingly assigned to the desorption of a less strongly bound mode of reactivity formed benzene (i.e., "tilted") generated on an initially crowded surface. The effect of surface chlorine is to increase the relative amount of reactively formed benzene desorbing at low temperature, with a concomitant narrowing and upward shift of the associated desorption peak. The overall scheme of hydrocarbon reactions can therefore be illustrated as shown in Scheme I.

Scheme I



Acknowledgment. C.H.P. thanks the Department of Education of Northern Ireland for the award of a research studentship. We are grateful for Johnson Matthey Ltd. for a loan of precious metals and to R. Stevenson for assistance with the synthesis of cyclobutadiene iron tricarbonyl.

Registry No. C_2H_2, 74-86-2; Pd, 7440-05-3.

Communications to the Editor

Isolation and X-ray Crystal Structure of the First Dinitrogen Complex of an f-Element Metal, $[(C_5Me_5)_2Sm]_2N_2$

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Since the discovery of the first dinitrogen complex,[1] $[Ru(NH_3)_5N_2]^{2+}$, there has been extensive research on the synthesis of N_2 complexes and the conversion of the N_2 ligand to NH_3.[2-5] Although many elements are now known to form dinitrogen complexes, a well-characterized N_2 complex of an f-element metal

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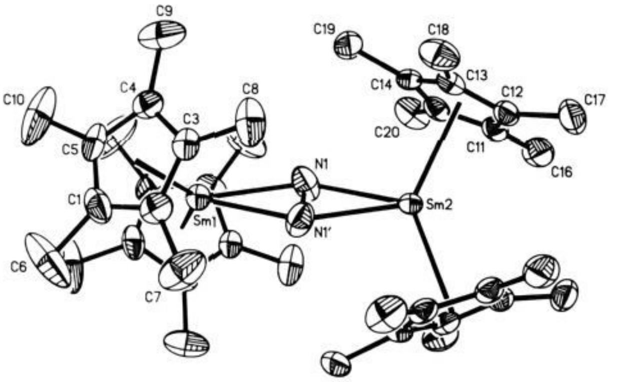

Figure 1. ORTEP diagram of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, **2**. Selected angles are Sm(1)–N(1)–Sm(2), 153.3 (3)°, N(1)–Sm(1)–N(1′), 26.8 (3)°, and Sm(1)–N(1)–N(1′), 76.6 (2)°.

has remained elusive. We report the first X-ray crystal structure of an f-element N_2 complex and a previously unknown type of metal dinitrogen coordination geometry.

Our earlier studies on the synthesis of the unusual bent metallocene $(C_5Me_5)_2Sm$, **1**,[6,7] by metal vapor methods gave evidence for a nitrogen-containing product in this system,[8,9] but definitive identification was not obtained. We find that slow crystallization of dark green **1** from toluene over a 4-week period gives a quantitative yield of dark, red-brown crystals of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, **2**,[10,11] Figure 1.[12] The N_2 unit and the two Sm atoms define a plane which contains a C_2 axis along the Sm(1)–Sm(2) vector. The Sm(1)–N(1) and Sm(2)–N(1) distances, 2.347 (6) and 2.368 (6) Å, respectively, are equivalent within experimental error.

To our knowledge this is the first example of planar, side-on bonding between two metals and a dinitrogen ligand.[2] Structurally, the closest examples are the systems $[(PhLi)_6Ni_2N_2(OEt_2)_2]_2$[13] and $[Ph_5Ni_2N_2Na_3Li_6(OEt)_4(OEt_2)_3]_2$[14] which have nonplanar side-on bonding with tetrahedral Ni_2N_2 units. Chemically, the early transition-metal complexes should be the most similar to **2**, but $[(C_5Me_5)_2ZrN_2]_2N_2$,[15] $[(C_5Me_5)_2Ti]_2N_2$,[16] and $[(C_5H_5)_2Ti(p\text{-}CH_3C_6H_4)]_2N_2$[17] display only end-on coordination of N_2 and $(C_{10}H_8)(C_5H_5)_5(C_5H_4)Ti_4(\mu_3\text{-}N_2)$[18] has an N_2 ligand side-bound to just one metal.

The Sm–N bond distances in **2** are in the 2.3–2.4 Å range found for Sm(III)–NR_2 bonds,[19,20] and the Sm–C(ring) distances[21] are in the 2.68–2.77 Å range typical for eight-coordinate Sm(III) complexes.[22] These distances and the C_5Me_5 shifts in the ^{13}C NMR spectrum[11] are consistent with the presence of Sm(III)[22] and a reduced N_2 unit. This is not consistent with the short N(1)–N(1′) distance of 1.088 (12) Å (cf. the 1.0975 Å distance in free N_2[23]).[24] A similar situation has been observed in the azobenzene derivative $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2Ph_2)$, **3**.[19,25] Complex **3** has a 1.25 (1) Å N–N distance similar to the 1.247 Å N=N bond in *trans*-azobenzene[26] even though each nitrogen is also connected to a phenyl group and a $(C_5Me_5)_2Sm$ unit which has structural and NMR features characteristic of a trivalent system. Hence, both **2** and **3** have N–N lengths shorter than expected based on the close approach of the $(C_5Me_5)_2Sm$ unit to the ligands. These features suggest that the bonding situation in **2** and **3** is not like that normally found in organosamarium complexes.

The four C_5Me_5 ring centroids in **2** define a tetrahedron in an arrangement like that in $[(C_5Me_5)_2Sm]_2(\mu\text{-}H)_2$, **4**.[27] In fact, **2** and **4** crystallize in the same space group and have very similar cell constants.[28] The structure of **4** was of theoretical interest[29] with regard to the positions of the hydride ligands, which were not located. Ligands attached to bent metallocenes generally lie in the plane which bisects the (ring centroid)–metal–(ring centroid) angle.[30] Since these planes are orthogonal in **4**, the hydride ligands cannot attain this configuration. The same situation occurs in **2** (the dihedral angle between the two centroid-Sm-centroid planes is 92.1°), but in this case, the ligand atoms were located. The nitrogen atoms lie in between the planes defined by each Sm atom and its two ring centroids, but the position is not symmetrical: the plane defined by Sm(1), N(1), N(1′), and Sm(2) forms an angle of 62.9° with the plane defined by Sm(1) and its ring centroids compared to a 45° angle for a symmetrical structure.[31]

After determining the structure of **2**, we examined its stability and the conditions under which it forms. When **2** is dissolved in toluene, N_2 gas is evolved; i.e., the formation of the dinitrogen complex is reversible, eq 1. When freshly sublimed **1**, which has

$$2(C_5Me_5)_2Sm + N_2 \xrightleftharpoons{\text{toluene}} [(C_5Me_5)_2Sm]_2N_2 \qquad (1)$$

been exposed as a solid to N_2, is placed in a Toepler pumping system (necessarily evacuated to 3×10^{-5} Torr) and toluene is added, 20% of the N_2 expected for pure **2** can be collected by Toepler pump. Analogous treatment of a sample of **1** which has been previously dissolved in toluene under N_2 releases 60% of the N_2 expected from **2**. After **2** is placed under 9.5×10^{-6} Torr for 4 h at ambient temperature, no gas is collected upon dissolution.

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(10) Slow crystallization is important. Crystallization over a 3-day period gives a mixture of dark green and dark red-brown crystals of **1** and **2**, respectively. Depending on the concentration, pure **2** also can be obtained from crystallizations over a 2-week period.

(11) Anal. Calcd for $Sm_2C_{40}H_{60}N_2$: Sm, 34.58; C, 55.25; H, 6.95; N, 3.22. Found for crystals of **2**: Sm, 34.95; C, 54.90; H, 7.03; N, 2.94. Found for a powder sample of **2**: Sm, 34.70; C, 54.94; H, 6.91; N, 2.91. ^1H NMR (C_7D_8, −20 °C) δ − 0.641 (s); ^{13}C NMR (C_7D_8 −20 °C) δ 111.86 (s, C_5Me_5), 27.47 (q, J_{CH} = 124 Hz, $C_5\mathit{Me}_5$); IR (KBr) 2960 vs, 2910 vs, 2850 vs, 1440 s, 1380 m, 1020 m cm^{-1}. A sample prepared from $^{15}N_2$ displays an identical IR spectrum.

(12) **2** crystallizes in space group $C2/c$ (C^6_{2h}; no. 15) with a = 16.524 (3) Å, b = 14.701 (2) Å, c = 17.046 (3) Å, β = 106.68 (1)°, V = 3966 (1) Å^3, and D_{calcd} = 1.46 g cm^{-3} for Z = 4. Least-squares refinement of the model based on 3155 reflections ($F^2 > 3.0\sigma(F^2)$) converged to a final R_F = 3.2% and R_{wF} = 4.9%. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions with d(C–H) = 0.95 Å.

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(20) Sm(III) ←NR_3 donor bonds are typically in the 2.5–2.8 Å range,[19] and Sm(II) ←NR_3 donor bonds would be even longer.

(21) The Sm–C(ring) range in **2** is 2.685(6)–2.768(6) Å with an average of 2.73 (2) Å.

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(24) In some cases, X-ray studies underestimate the N–N length in dinitrogen complexes due to thermal motion.[2] The thermal ellipsoids in **2** are not oriented in a direction which would cause this to happen.

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(28) Compare footnote 12 with the cell constants for **4**: a = 16.532 (6) Å, b = 14.260 (4) Å, c = 16.948 (4) Å, β = 104.26 (4)°, V = 3782.3 Å^3.

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(31) Compare with the symmetric arrangement of the μ-hydride positions in $[(C_5Me_5)_2ThH(\mu\text{-}H)]_2$. Broach, R. W.; Schultz, A. J.; Williams, J. M.; Brown, G. M.; Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Science (Washington, D.C.)* **1979**, *203*, 172–174.

Hence, **1** will react with N_2 to some extent in the solid state, and solid **2** releases its N_2 when placed under vacuum for several hours. Complex **2** is best formed by precipitation from solutions of **1** under N_2.[10]

NMR experiments reveal a temperature-dependent equilibrium between **1** and **2** in solution. The ^{1}H NMR spectrum of **1** prepared in the absence of N_2 contains a single C_5Me_5 resonance in the normal region.[32] After the sample is exposed to N_2, the NMR spectrum contains a small second peak at −0.6 ppm attributed to **2** (ratio of **1**:**2** is approximately 40:1). As the temperatue is decreased, the concentration of **2** increases, but complete conversion of **1** to **2** is not achieved.[33]

The high reactivity of Sm(II)[34-36] and the open coordination environment of $(C_5Me_5)_2Sm$[6,7,34,37] make this molecule one of the most likely f-element systems to form a complex with N_2. Definitive identification of the dinitrogen complex has been difficult due to the delicate balance in the equilibrium in eq 1.[38] The reactivity of the N_2 ligand in the unique planar $M(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)M$ environment in **2** is under study.

Acknowledgment. We thank the National Science Foundation for support of this research.

Registry No. 1, 90866-66-3; **2**, 115244-63-8; N_2, 7727-37-9.

Supplementary Material Available: Tables of positional parameters, bond distances and angles, and thermal parameters (3 pages); table of observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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(32) δ 1-2 ppm. The peak position is concentration dependent.

(33) At −20 °C the ratio of **1** to **2** is approximately 3.5:1.

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(38) This is similar to the $(C_5Me_5)_2Sm$ + $(C_5Me_5)_2Sm(C_5H_5)$ → $(C_5Me_5)_2Sm^{II}(\mu\text{-}C_5H_5)Sm^{III}(C_5Me_5)_2$ system.[22]

β-Lactams from Ester Enolates and Silylimines: Enantioselective Synthesis of (+)-PS-5

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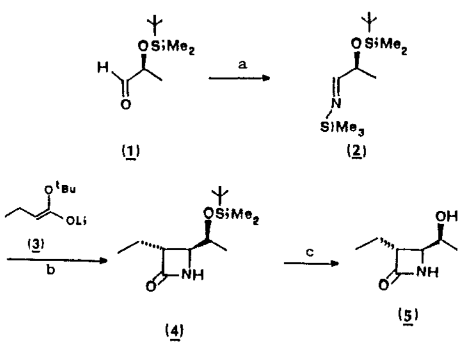
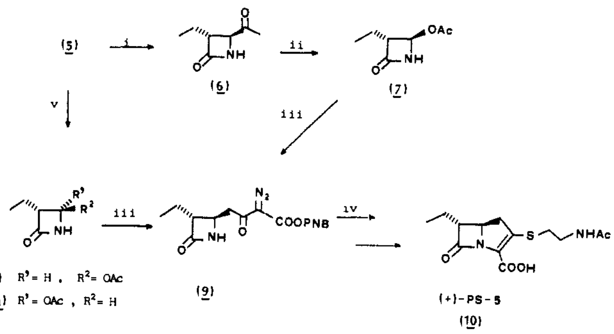
Received April 13, 1988

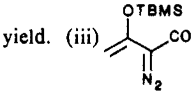
Scheme I[a]



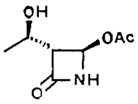
[a] (a) LiN$(SiMe_3)_2$, THF, −40 °C. (b) THF, −78 °C, 15 min, room temperature, 8 h, 61% yield. (c) CH_3CN, HF catalyst, 90 min, 97% yield.

Scheme II[a]



[a] (i) Et_2O, H_2CrO_4, 2 h, room temperature, 76% yield. (ii) MCPBA, EtOAc, 3 h, 50 °C, 72% yield. (iii)  /$ZnCl_2$. (**8**) (iv) Reference 4h. (v) $Pb(OAc)_4$, $CaCO_3$, benzene, 3 h, reflux, 61% yield.

In the course of a general project on the stereocontrolled synthesis of β-lactam antibiotics, we[1] and others[2] recently have demonstrated the versatility of the ester-imine condensation in the production of the azetidin-2-one ring. Through this approach, we have been able to synthesize the optically active 3-(1′-hydroxyethyl)-azetidin-2-one (A),[1a] the key intermediate in the synthesis of thienamycin and related β-lactam antibiotics.[3a] In that synthesis (*S*)-(+)-ethyl 3-hydroxybutanoate was utilized to induce the correct absolute stereochemistry at carbon 3, of the β-lactam ring, in the ester enolate-imine condensation.



(A)

We now report a new enantioselective total synthesis of the carbapenem (+)-PS-5 **10**,[4] in which an optically active silylimine

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