ligands as is the case with $(\eta\text{-}C_5H_5)_2W$[24] and $Ru(Me_2PCH_2CH_2PMe_2)_2$[25] or in the more familiar intramolecular processes such as orthometalation.[10a] Methyl substituents on the cyclopentadienyl ligand in $[(\eta\text{-}C_5Me_5)Ir(CO)]$ may make self-metalation less likely while at the same time increasing the electron density on iridium somewhat.[26]

The factors involved will become clearer as other complexes are found to which the C–H bonds of paraffins will readily add. We are seeking further examples among other metals of the third transition series, where we expect the energetics of the process to be most favorable and the products most stable. The work is being carried out in conjunction with our investigation of the hydrogen-mediated photolysis of similar complexes.[27]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for generous financial support.

Registry No. 1, 32660-96-1; **2**, 81753-14-2; **3**, 81753-15-3; **4**, 81753-16-4; **5**, 81753-17-5; **6**, 81753-18-6; **7**, 32609-75-9; neopentane, 463-82-1; cyclohexane, 110-82-7; benzene, 71-43-2.

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(24) Berry, M.; Cooper, J. N.; Green, M. L. H.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1980**, 29.

(25) (a) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1965**, 843. (b) Cotton, F. A.; Hunter, D. L.; Frenz, B. A. *Inorg. Chim. Acta* **1975**, *15*, 155.

(26) The behavior of $(\eta\text{-}C_5H_5)Ir(CO)_2$ upon irradiation in alkanes is of obvious interest.

(27) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.*, preceding communication in this issue.

Tertiary Phosphine Complexes of the f-Block Metals. Crystal Structure of $Yb[N(SiMe_3)_2]_2[Me_2PCH_2CH_2PMe_2]$: Evidence for a Ytterbium-γ-Carbon Interaction

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The 4f-block metals have a rich coordination chemistry with nitrogen and oxygen ligands.[1a] In contrast only one example of a tertiary phosphine complex of a lanthanide metal, Cp_3YbPPh_3, has been claimed.[1b-f] Lanthanide ions are generally thought to be examples of class A[1g] or hard[1h] Lewis acids. Thus, the most thermodynamically stable complexes are formed between nitrogen and oxygen donors and lanthanide acceptors rather than between phosphorus and sulfur donors. The isolation of phosphine complexes of the actinide metals (thorium and uranium) of the type $MX_4(dmpe)_2$, where dmpe is 1,2-bis(dimethylphosphino)ethane and X is halide, alkyl, or phenoxide,[2a] and $U(Me_5C_5)_2H(dmpe)$[2b] suggests that phosphine complexes of the lanthanide metals should be isolable. A synthetic route to such compounds would seem to require lanthanide complexes with empty coordination sites or ligands that are readily displaced by tertiary phosphines.

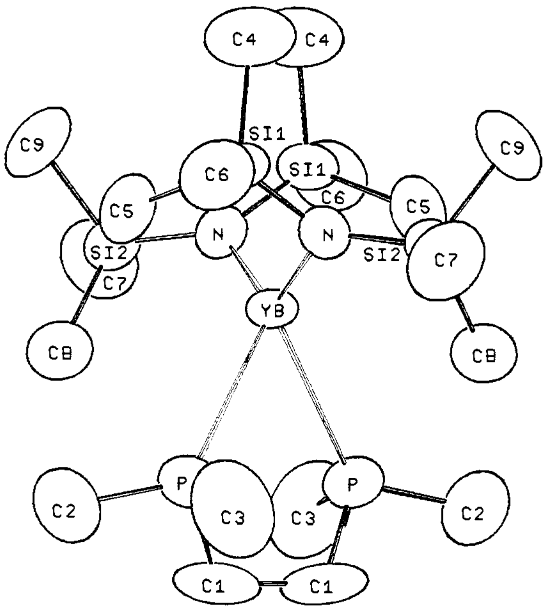

Figure 1. ORTEP diagram of $Yb[N(SiMe_3)_2]_2(dmpe)$. Some bond lengths and bond angles are as follows: Yb–N, 2.331 (13) Å; Yb–P, 3.012 (4) Å; N–Yb–N, 123.6 (6)°; P–Yb–P, 68.4 (2)°; N–Yb–P, 101.2 (3)°.

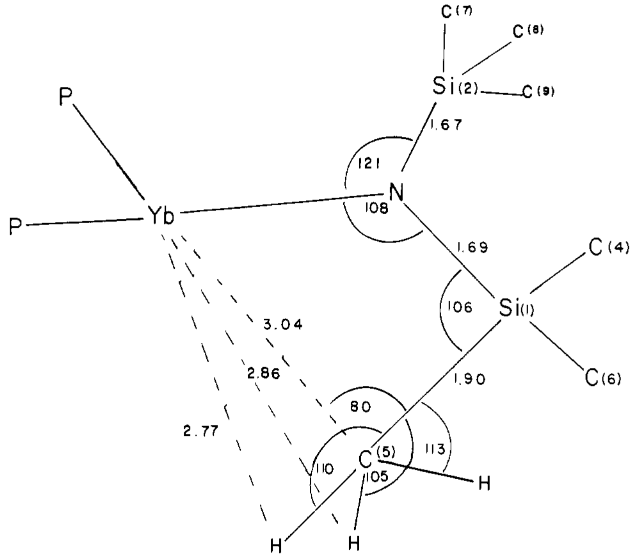

Figure 2. Line drawing showing the Yb–C(5) interaction. The bond angles are in degrees and the bond lengths are in angstroms.

We have described a preparation of the divalent $Eu[N(SiMe_3)_2]_2L_2$, where L = tetrahydrofuran or 1,2-dimethoxyethane, that utilizes sodium naphthalene as a reducing agent.[3] This synthetic method is only applicable in relatively strong donor solvents and was unsuccessful in the preparation of ytterbium(II) derivatives. A much improved synthetic scheme, which allows preparation of europium(II) and ytterbium(II) silylamides in the weak donor solvent diethyl ether, is shown in eq 1.

$$\mathrm{YbI_2 + 2NaN(SiMe_3)_2 \xrightarrow{OEt_2} \underset{I}{Yb[N(SiMe_3)_2]_2(OEt_2)_2}}$$

$$\mathrm{EuI_2 + 2NaN(SiMe_3)_2 \xrightarrow{OEt_2} \underset{II}{NaEu[N(SiMe_3)_2]_3}} \qquad (1)$$

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*Address correspondence to this author at the Chemistry Department.

(1) (a) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; pp 981–1004. (b) Fischer, E. O.; Fischer, H. *J. Organomet. Chem.* **1966**, *6*, 141–148. (c) McAuliffe, C. A., Ed. "Transition Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands"; Halsted Press: New York, 1973; p 36. (d) McAuliffe, C. A.; Levason, W. "Phosphine, Arsine, and Stibine Complexes of the Transition Metals"; Elsevier: New York, 1979; pp 72, 215. (e) The scandium complexes of 1,2-bis(diphenylphosphino)ethane, $ScCl_3(dppe)$ and $ScBr_3(dppe)_{1.5}$, have been described: Greenwood, N. N.; Tranter, R. L. *J. Chem. Soc. A* **1969**, 2878–2883. (f) A solution interaction between $P\text{-}n\text{-}Bu_3$ and $YbCp_3$ has been suggested on the basis of ^1H NMR data: Marks, T. J.; Porter, R.; Kristoff, J. S.; Shriver, D. F. In "Nuclear Magnetic Resonance Shift Reagents"; Sievers, R. E., Ed.; Academic Press: New York, 1973; p 247. (g) Ahrland, S.; Chatt, J.; Davies, N. R. *Q. Rev., Chem. Soc.* **1958**, *12*, 265–276. (h) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539.

(2) (a) Edwards, P. G.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1981**, *103*, 7792–7794. (b) Duttera, M. R.; Fagan, P. J.; Marks, T. J.; Day, V. W. *Ibid.* **1982**, *104*, 865–867. Marks (Marks, T. J. 28th IUPAC Congress, Vancouver, Canada, August 17, 1981) described the synthesis and X-ray structure of $U(Me_5C_5)_2(dmpe)$.

(3) Tilley, T. D.; Zalkin, A.; Andersen, R. A.; Templeton, D. H. *Inorg. Chem.* **1981**, *20*, 551–554.

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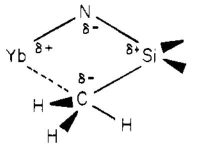
The type of product isolated is metal dependent. With ytterbium, crystallization from diethyl ether yields the bis(diethyl ether) complex I,[4] whereas for europium, similar crystallization conditions give the anionic complex II.[5] The different types of complexes can be explained by noting that in a given coordination number, the ionic radius of Eu(II) is ca. 0.1 Å greater than that of Yb(II).[6] Since two diethyl molecules are less sterically demanding than a silylamide group, the latter is more readily accommodated about the coordination sphere of the larger Eu(II) ion. The preparation of pentane-soluble complexes of $M[N(SiMe_3)_2]_2$, where M = Eu or Yb, with the relatively weak donor ligands $[N(SiMe_3)_2]^-$ or OEt_2 results in suitable reagents for preparation of phosphine complexes of $M[N(SiMe_3)_2]_2$ by way of displacement reactions.

The coordinated diethyl ether in I is displaced by 1,2-(dimethylphosphino)ethane (dmpe), giving purple, diamagnetic $Yb[N(SiMe_3)_2]_2(dmpe)$.[7] An ORTEP drawing is shown in Figure 1.[9] As this is the first lanthanide phosphine complex to be structurally characterized, no bond-length data are available for comparison.

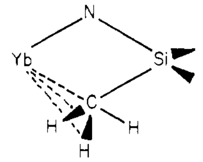
Inspection of the bond distances and angles (Figure 2) in the $N(SiMe_3)_2$ ligands, which are related by 2-fold molecular symmetry, reveals distortions that results from an interaction between the C(5) methyl group and the ytterbium atom as shown in Figure 2. The Yb–N–Si(1) bond angle of 108.5 (6)° is less than the Yb–N–Si(2) angle of 121.0 (7)°. The latter angle is normal since it lies in the range found for other metal silylamides (121.5 ± 4.5°).[10] In addition the N–Si(1)–C(5) angle of 106.3 (7)° is smaller than the other N–Si(1)–C(4,6) and N–Si(2)–C(7–9) angles, which average to 115.4 ± 0.8 and 112.1 ± 1.5°, respectively. This is accompanied by an opening of the Si(1)–N–Si(2) angle to 130.5 (8)°, which is larger than is observed in metal silylamides, which average to 119.5 ± 3.6°.[10] The Yb–C(5) interaction appears to lengthen the bond distances within the incipient metallacyclic ring [YbNSi(1)C(5)] relative to the normal YbNSiC(Me) group, though these bond length differences are not statistically significant. Thus, the N–Si(1) distance of 1.691 (13) Å is equal to that of the N–Si(2) distance of 1.667 (13) Å. Further, the Si(1)–C(5) distance of 1.896 (20) Å is not significantly different from the other two Si(1)–C(Me) distances of 1.861 (20) and 1.872 (16) Å.

The Yb–C(5) separation is less than the sum of the van der Waals radius of a methyl group (2.0 Å) and the divalent metallic radius of ytterbium (1.7 Å)[11] but longer than the Yb(III)–C(methyl) distances of 2.57 Å in $[Cp_2Yb(\mu\text{-}Me)]_2$.[12a] Thus, the C(5) carbon atom and two of the three hydrogen atoms bonded to it are closer than expected to the metal atom. These three hydrogens were located and refined isotropically to reasonable tetrahedral positions about C(5), and no distortion due to the presence of the ytterbium was observed. The Yb–H distances refined to 2.76 (8), 2.85 (6), and 3.18 (1) Å, and the H–C(5)–H bond angles are 110, 105, and 113°, as shown in Figure 2.

Geometrically, the ytterbium–C(5) methyl interaction resembles the situation observed for compounds in which a methyl group bridges two metals, i.e., $[Cp_2Y(\mu\text{-}Me)]_2$,[12a] $[Cp_2Yb(\mu\text{-}Me)]_2$,[12a] $[Cp_2Yb(\mu\text{-}Me)_2AlMe_2]$,[12b] and $Me_4(\mu\text{-}Me)_2Al_2$.[12c] In $[Cp_2Y(\mu\text{-}Me)]_2$ and $Me_4(\mu\text{-}Me)_2Al_2$ the hydrogen atoms on the methyl groups were located, and they point away from the metal atoms, ruling out a direct metal–hydrogen interaction. the M–(μ-C)–M angles in these alkyls are 87° in $[Cp_2Yb(\mu\text{-}Me)]_2$, 88° in $[Cp_2Y(\mu\text{-}Me)]_2$, 83 and 78° in $[Cp_2Yb(\mu\text{-}Me)_2AlMe_2]$, and 76° in $Me_4(\mu\text{-}Me)_2Al_2$. The Yb···C(5)Si(1) angle is 79.9 (7)° in $Yb[N(SiMe_3)_2]_2(dmpe)$. It is therefore appealing to view the Yb-methyl group as semibridging the electropositive ytterbium atom. The postulate that the interaction is primarily due to a metal–carbon rather than a metal–hydrogen interaction is consistent with the expected charge distribution (on the basis of relative electronegativity values) shown in A. This is in contrast to the situation found in transition metals in which M···HC interactions are observed.[13] Though the X-ray data are consistent with a Yb···C(5) interaction rather than a Yb···H interaction, it is not inconsistent with a multicenter interaction (B) where the pairs of electrons of the C–H bond are interacting with the ytterbium atom. Futher speculation on this point is meaningless in the absence of a neutron diffraction study.



A



B

These models for the two-center Yb···C or multicenter Yb···CH_2 interactions in $Yb[N(SiMe_3)_2]_2[dmpe]$ are important in defining the role of the metal atom in $[(Me_3Si)_2N]_3MMe$ (M = Th, U) compounds in activating the γ-hydrogen atoms on the silylamide ligands.[14] The M···CH_3 interaction should increase the acidity of the hydrogen atom on the methyl group, promoting alkane elimination through a four-center transition state, as previously described. Therefore, a M···CH_3Si interaction may be important in metallacycle formation, and an oxidative addition process, which is doubtless endothermic for these tetravalent metals, is not required.

The anionic europium complex, II, also undergoes reaction with dmpe, giving an orange, paramagnetic complex of empirical formula $Eu[N(SiMe_3)_2]_2(dmpe)_{1.5}$.[15] The europium complex,

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(4) Orange crystals from diethyl ether (−70 °C), mp 69–71 °C; ^{1}H NMR (26 °C, PhH-d_6) δ 0.41 (s, 36 H, $N(SiMe_3)_2$), 1.06 (t, J = 7 Hz, 12 H, OCH_2CH_3), 3.51 (q, J = 7 Hz, 8 H, OCH_2CH_3); $^{13}C\{^1H\}$ NMR (26 °C, PhH-d_6) δ 5.57 ($N(SiMe_3)_2$), 14.7 (OCH_2CH_3), 65.2 (OCH_2CH_3).

(5) Yellow needles from diethyl ether (−70 °C), mp 152–153 °C. The crystal structure of this complex has been completed and will be described later; Zalkin, A., unpublished results.

(6) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32A*, 751–767.

(7) Purple prisms from pentane (−10 °C), mp 195–197 °C; ^{1}H NMR (26 °C, PhH-d_6) δ 0.46 (s, 36 H, $N(SiMe_3)_2$), 0.86 (apparent s, 12 H, PMe_2), 1.04 (a three-line pattern, with the separation of the outermost lines being 13 Hz,[8] 4 H, PCH_2); $^{13}C\{^1H\}$ NMR (26 °C, PhH-d_6) δ 5.75 ($N(SiMe_3)_2$), 11.6 (apparent s, PMe_2); 25.8 (apparent three-line pattern with a separation between the outermost lines of 8 Hz). The spin system of dmpe in the ^{1}H NMR spectrum is $X_6AY_2Y_2'A'X_6'$ and in the $^{13}C\{^1H\}$ NMR spectrum is ABX. Accordingly, a first-order analysis is inappropriate.[8] $^{31}P\{^1H\}$ NMR (26 °C, PhH-d_6) δ −40.9. The coordination chemical shift, defined as the chemical shift of the complex less that of the free ligand, is 8.5 ppm.

(8) (a) Akhtar, M.; Ellis, P. D.; MacDiarmid, A. G.; Odom, J. D. *Inorg. Chem.* **1972**, *11*, 2917–2921. (b) Aime, S.; Harris, R. K.; McVicker, E. M.; Fild, M. *J. Chem. Soc., Dalton Trans.* **1976**, 2144–2153.

(9) The compound crystallizes in the orthorhombic space group *F2dd* (C_{2v}^{19}) with cell dimensions $a = 11.353$ (2), $b = 18.704$ (5), and $c = 31.084$ (8) Å with $Z = 8$ and $d_{calcd} = 1.296$ g cm^{-3}. The data were collected on a Nonius CAD-4 automated diffractometer with Mo Kα X-rays (λ = 0.709 30 Å). The data were corrected for absorption (μ = 22.6 cm^{-1}). The structure was solved from Patterson and electron density maps and refined by full-matrix least-squares to a conventional *R* factor of 0.050 by using 1916 data where $F^2 > (\sigma(F))^2$. The handedness of the structure was checked by reversing the sign of the anomalous dispersion terms. The resulting difference in the *R* factor was insignificant, which could be due to either a lack of precision in the data, undetected twinning, or both. A referee has suggested that the dmpe ligand suffers from partial disorder. We see no disorder in the electron density maps. The C(1)–C(1)′ bond distance of 1.48 ± 0.05 Å is a valid single bond within the statistics.

(10) (a) Andersen, R. A.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1978**, *17*, 2317–2319. (b) Tilley, T. D.; Zalkin, A.; Andersen, R. A.; Templeton, D. H. *Ibid.* **1981**, *20*, 551–554. (c) Andersen, R. A.; Zalkin, A.; Templeton, D. H. *Ibid.* **1981**, *20*, 622–623. (d) McCullough, L. G.; Turner, H. W.; Andersen, R. A.; Zalkin, A.; Templeton, D. H. *Ibid.* **1981**, *20*, 2869–2871. (e) Hursthouse, M. B.; Rodesiler, P. F. *J. Chem. Soc., Dalton Trans.* **1972**, 2100–2102. (f) Airoldi, C.; Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Malik, K. M. A.; Raithby, P. R. *Ibid.* **1980**, 2010–2015.

(11) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(12) (a) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45–53. (b) *Ibid.* **1979**, 54–61. (c) Huffman, J. C.; Streib, W. E. *J. Chem. Soc., Chem. Commun.* **1971**, 911–912.

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(14) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 7728–7729; *Inorg. Chem.* **1981**, *20*, 2991–2995.

II, and the ytterbium complex, I, yield 2:1 complexes with tri-*n*-butylphosphine of composition $M[N(SiMe_3)_2]_2(P\text{-}n\text{-}Bu_3)_2$, where M is Eu[16] or Yb.[17]

Acknowledgment. This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under contract number W-7405-Eng-48. We also thank Dr. F. J. Hollander, staff crystallographer of the U.C. Berkeley X-ray facility (CHEXRAY), for collecting X-ray data.

Registry No. I, 81770-53-8; II, 81802-35-9; $Yb[N(SiMe_3)_2](dmpe)$, 81770-54-9; $Eu[N(SiMe_3)_2]_2(dmpe)_{1.5}$, 81770-55-0; $Eu[N(SiMe_3)_2]_2(P\text{-}n\text{-}Bu_3)_2$, 81770-56-1; $Yb[N(SiMe_3)_2]_2(P\text{-}n\text{-}Bu_3)_2$, 81770-57-2.

Supplementary Material Available: Positional and thermal parameters and structure factors with their estimated standard deviations (10 pages). Ordering information is given on any current masthead page.

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[15] Orange prisms from pentane (−10 °C). Anal. Calcd for $C_{21}H_{60}N_2EuP_3Si_4$: C, 36.1; H, 8.67; N, 4.01; P, 13.13. Found: C, 35.4, H, 8.34, N, 3.80; P, 13.0. The ^1H NMR spectrum of a benzene extract of a solution of the complex that had been hydrolyzed with D_2O showed resonances due to $DN(SiMe_3)_2$ and dmpe in area ratio 2:1.5.

[16] Orange crystals from pentane (−70 °C), mp 48–49 °C. Anal. Calcd for $C_{36}H_{90}N_2EuP_2Si_4$: C, 49.3, H, 10.3; N, 3.19; P, 7.06. Found: C, 49.0; H, 10.2; N, 2.79; P, 6.82. The paramagnetic complex, 7.4 μ_B (Evan's method, 30 °C, PhH), was hydrolyzed with water, and the ^1H NMR of an aliquot in benzene gave resonances due to $(Me_3Si)_2NH$ and $P\text{-}n\text{-}Bu_3$ in a 1:1 area ratio.

[17] Brown-red prisms from pentane (−70 °C), mp 46–48 °C. Anal. Calcd for $C_{36}H_{90}N_2P_2Si_4Yb$: C, 48.1; H, 10.1; N, 3.12; P, 6.89. Found: C, 48.8; H, 10.0; N, 2.87; P, 7.47. ^1H NMR (26 °C, PhH-d_6) δ 0.48 (s, 36 H, $N(SiMe_3)_2$), 1.00 (an apparent t with the separation between the outermost lines being 12 Hz, 18 H, $P(CH_2CH_2CH_2C\mathit{H}_3)_3$), 1.49 (an apparent s, 36 H, $P(C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2CH_3)_3$); $^{13}C\{^1H\}$ NMR (26 °C, PhH-d_6) δ 6.27 (s, $N(SiMe_3)_2$), 14.0 (an apparent s due to the γ-C of $P\text{-}n\text{-}Bu_3$), three apparent doublets at 24.9 (separation of 10 Hz), 26.9 (separation of 10 Hz), 28.3 (separation of 11 Hz due to the other three carbon atoms); $^{31}P\{^1H\}$ NMR (26 °C, PhH-d_6) δ −29.6. The coordination chemical shift is zero.

Palladium(0)-Catalyzed Allylic Alkylation and Amination of Allylnitroalkanes

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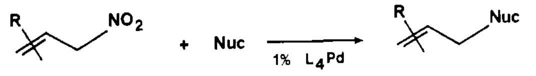
Received March 24, 1982

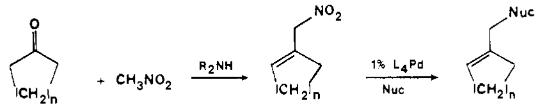
The chemistry of nitroalkanes has been the subject of considerable recent development. Nitro-stabilized carbanions effected substitution reactions with benzyl halides, tosylates, and nitro compounds, resulting primarily in C-alkylation of the carbanion.[1,2] In a related process, nitroalkyl anions effected the displacement of a nitro group from α-nitro esters, α-nitro ketones, α-nitro nitriles, and α,α-dinitro compounds.[3] α-Halonitroalkanes and *gem*-dinitroalkanes underwent displacement of a halide or nitro group, respectively, when treated with stabilized carbanions[4–6] or thiolate anions.[7] The ease of replacement of a nitro group by hydrogen with use of the sodium salt of methanethiol,[8] trialkyltin hydrides,[9,10] or 1-benzyl-1,4-dihydronicotinamide[11] has significantly increased the synthetic utility of nitroalkanes. All of these reactions are thought to proceed by electron-transfer radical chain processes.

In contrast, the anion of (phenylsulfonyl)nitromethane[12a] and other nitroalkanes[2,12b] cleanly alkylated allylic acetates in the presence of 10–20% of tetrakis(triphenylphosphine)palladium, in a process presumed to be a straightforward nucleophilic attack on a π-allylpalladium complex intermediate.[13–15] In this paper we report the use of allylic nitro compounds as *substrates* for palladium(0)-catalyzed allylic alkylation and amination reactions (eq 1). These results, summarized in Table I, make the extensive chemistry of π-allylpalladium complexes[16] accessible to a new class of allylic substrates.



(1)

Cyclic allylic nitro compounds were readily available from the reaction of cyclic ketones, nitromethane, and an amine.[17,18] These reacted readily with stabilized carbanions and amines in the presence of 1% L_4Pd to result in allylic alkylation or amination in good yield and without allylic transposition (eq 2). The anion of ethyl cyanoacetate underwent substantial dialkylation, as is typical for this carbanion. The cyclohexenyl substrate **1b** was considerably less reactive than either **1a** or **1c** and required prolonged heating in Me_2SO to effect reaction. Under these conditions, some decarboxylation was observed.



(2)

n = 2 **1a**
n = 3 **1b**
n = 4 **1c**

Acyclic allylnitro compounds were not available from the condensation of a nitroalkane carbanion with aldehydes or ketones since the vinylnitro compound was the sole product from reactions of this type because of facile isomerization.[19–21] In the hopes that the allylnitro compound would be in equilibrium with the vinylnitro compound under basic conditions, 2-nitro-2-butene (from nitroethane and acetaldehyde) was treated with dimethyl sodiomalonate and the usual palladium(0) catalyst. However, only Michael addition of the enolate to the vinylnitro compound was observed. A solution to this problem was offered by the observation that the anion of **1a** reacted with dimethyl malonate itself (in the presence of a palladium(0) catalyst) to give a 69% yield of this allylic alkylation product. This indicates that the nitro-stabilized anion, although a much weaker base, was in equilibrium with

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[1] For a review see N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, **14**, 734 (1975).

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[8] N. Kornblum, S. C. Carlson, and R. G. Smith, *J. Am. Chem. Soc.*, **101**, 647 (1979).

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