Conversion of aryl azides on nickel centers into tetraazadiene-nickel complexes [Ni0(Ar2N4)2], [CpNiI(Ar2N4)], and [(RNC)2Ni0(Ar2N4)]. Crystal structure of [Ni0{1,4-(3,5-Me2C6H3)2N…

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(13) The average bonding M–M distance follows: Pd, 2.750; Pt, 2.760 Å. The average M–P distance follows: Pd, 2.315; Pt, 2.27 Å. The angle defined by the two planes formed by three metal atoms follows: Pd, 93; Pt, 97° The nonbonding distances follow: Pd, 3.365; Pt, 3.548 Å.

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J. Dubrawski, J. C. Kriege-Simondsen, R. D. Feltham*

Department of Chemistry, The University of Arizona
Tucson, Arizona 85721

Conversion of Aryl Azides on Ni Centers into Tetraazadiene–Nickel Complexes [Ni⁰(Ar₂N₄)₂], [CpNiᴵ(Ar₂N₄)], and [(RNC)₂Ni⁰(Ar₂N₄)]. Crystal Structure of [Ni⁰{1,4-(3,5-Me₂C₆H₃)₂N₄}₂]

Sir:

In contrast to the versatile coordination chemistry of the α-diimine ligand, RNCHCHNR, which can act as a σ,σ-N,N-chelating,[1a,2a] σ,σ'-N,N-[2b,3] or σ-N,η²-CN-bridging,[1b] or as a σ-N-monodentate[3]-bonded ligand, only a few metal complexes of the isostructural tetraazadiene ligand, RNNNNR, are known.[4] These are 1:1 complexes with the tetraazadiene ligand σ bonded via the 1,4-nitrogen atoms. The reason for this contrast between α-diimine and tetraazadiene chemistry seems to be the fact that the RN₄R ligand, which apparently does not exist as a free compound, has to be generated directly at the metal center and subsequently stabilized by coordination.

We report here the first example of a bis(tetraazadiene) metal complex, [Ni⁰(ArN₄Ar)₂], which is the counterpart of the [bis(α-diimine)nickel(0)][5] complexes in α-diimine–metal chemistry. We also describe the stepwise synthesis of [Ni(ArN₄Ar)₂] from [Cp₂Ni] via novel [CpNiᴵ(ArN₄Ar)].

Pure [Ni(ArN₄Ar)₂] [Ar = 4-MeC₆H₄ (I), 4-MeOC₆H₄ (II), 3,5-Me₂C₆H₃ (III)][6] was isolated in 20–25% yield from the reaction of [Ni(COD)₂] with ArN₃ (1:4 molar ratio) in toluene. The reaction was carried out at room temperature and is exothermic. The dark purple colored solids I–III are diamagnetic as indicated by their ¹H NMR solution spectra.[7]

It has been pointed out[8,9] that the tetraazadiene ligand can be bonded in two ways represented by the formal valence structures A and B (Figure 1) which differ with respect to the formal oxidation state of the metal. To obtain information about the bonding in the diamagnetic [Ni(ArN₄Ar)₂] complexes, a single-crystal X-ray structure determination of III was carried out.[10] The molecular structure of the monomeric [(3,5-Me₂C₆H₃N₄C₆H₃Me₂-3,5)₂Ni] units (Figure 2) shows the following important features. There are two independent ArN₄Ar ligands coordinated to the Ni center via the 1,4-nitrogen atoms, so forming two N₄Ni chelate rings. Within each ArN₄Ar ligand both Ar rings and the N₄ unit lie in the same plane while the two N₄Ni chelate rings are mutually perpendicular. Therefore the Ni center has a pseudotetrahedral geometry.

The conjugated arrangement of the double bonds in the N₄ unit of canonical form A is ideally suited for interaction with the aryl π system which would result in multiple bond character in the N₄ unit as well as in the adjacent N–C bonds. These two features are observed in our compound, i.e., almost identical N–N bond distances [1.325 (3) and 1.319 (4) Å] and N–C distances of 1.426 (4) Å. In contrast, in the complex [(4-FC₆H₄N₄C₆H₄F-4)IrCO(PPh₃)₂]BF₄ the ArN₄Ar ligand contains dissimilar 1,2- and 2,3-N–N distances of 1.400 (16) and 1,270 (16) Å and C–N distances of 1.481 (18) and 1.456 (18) Å, with aryl rings which are noncoplanar with the N₄ unit.

This was interpreted as indicative of an ArN₄Ar valence structure of type B and hence an Ir d⁶ species.[8] The distinctive structural features of our tetrahedral [Ni(ArN₄Ar)₂] complexes support the view that they are best represented by a formal valence structure of type A and thus a Ni⁰ d¹⁰ (18e) electronic configuration.

The complexes I–III are stable in boiling toluene in air, whereas the related [Ni⁰(Ar-α-diimine)₂] complexes are extremely sensitive to oxidation and thermal decomposition.[5] This difference in stability might be due to a better π-accepting capability of the ArN₄Ar system.

The formation of the 18e [(ArN₄Ar)₂Ni⁰] systems with normal aromatic azides is surprising in view of the report by Stone et al. that pentafluorophenyl azide (C₆F₅N₃) reacts with [Ni(COD)₂] to yield the monotetraazadiene complex [(C₆F₅N₄C₆F₅)Ni(COD)] (IV).[9]

Reactions of I with HCl, CH₂Cl₂, and CHCl₃ resulted in formation of as yet unidentified products.[11] Reaction of I with excess t-BuNC in boiling toluene resulted in formation of [(t-BuNC)₂Ni(4-MeC₆H₄N₄C₆H₄Me-4)] (V),[12] whereas I failed to react with CO, PPh₃, and bpy, which were likewise expected to result in formation of complexes [L₂Ni(ArN₄Ar)]. Since these substitution reactions failed the reaction of I with t-BuNC probably involves attack of an RNC molecule on one of the coordinated ArN₄Ar ligands followed by stabilization of the resulting labile [(Ar₂N₄)Ni⁰] species by coordination with RNC.

The reaction of [Cp₂Ni] (20e species) with excess 4-MeC₆H₄N₃ in boiling toluene is still incomplete after 35 min.[13] Workup of the reaction mixture resulted in the isolation of black microcrystals, [CpNi{(4-MeC₆H₄)₂N₄}][14] (VI, 10% yield), in addition to unreacted [Cp₂Ni] (40%) and [Ni⁰{(4-MeC₆H₄)₂N₄}₂] (5%). Compound VI is paramagnetic and ESR spectra are consistent with the formulation of this compound as a Niᴵ species with a monomeric structure[15] and with a σ,σ-N,N-chelate-bonded (4-MeC₆H₄)₂N₄ ligand.[16]

The similarity of the IR spectra in the ligand vibration region of VI and the known monomeric [CpCo{(4-MeC₆H₄)₂N₄}] (VII)[14,17,18] strongly indicates that both compounds are isostructural. Accepting that the Cp ring in VI is pentahapto bonded and the ArN₄Ar group acts as a (4e) σ,σ-N,N-chelating ligand (formal valence structure A), [CpNi{(4-MeC₆H₄)₂N₄}] must be formulated as a 19e Niᴵ species.[19] Using similar arguments, VII, which is diamagnetic, is an 18e Coᴵ species.

Support for the 19e configuration comes from the observation that reaction of pure VI in boiling toluene (2 h) with 2 equiv of 4-MeC₆H₄N₃ gives rise to 18e [Ni⁰{(4-MeC₆H₄)₂N₄}₂] (52% yield), while reaction of VI with 2 equiv of t-BuNC at room temperature yields [(t-BuNC)₂Ni(4-MeC₆H₄N₄C₆H₄Me-4)] (V, 80% yield). In contrast, [CpCo{(4-MeC₆H₄)₂N₄}] is unreactive toward excess ArN₃ or t-BuNC.

Considerable interest exists in these ArN₄Ar nitrogen ligands because they can be generated both from aryl azides via metal nitrenes followed by 1,3-dipolar addition reactions[4] or from metal–diazonium intermediates. Such species are postulated in schemes which describe the interaction and conversion of dinitrogen on metal centers.[4] In this respect the formation of I–III and VI is of interest because of the possible involvement of species of the type IX–XIII: [(COD)NiNAr] (IX), [(COD)NiN₄Ar₂] (X), [ArNNiNAr] (XI), [ArNNiN₄Ar₂] (XII), or [CpNiNAr] (XIII).

Dinitrene species have recently been structurally characterized, i.e., [Cp₂Mo₂S₂(NR)₂][20] and cis-[Mo(NC₆H₅)₂-DTC₂].[21] In the [Ni(COD)₂]–ArN₃ reactions polymeric material is formed which might be due to polymerization of species of the type XI, since in the bent form the nitrene can readily act as a bridging species. The formation of [Ni⁰(Ar-

Figure 1.

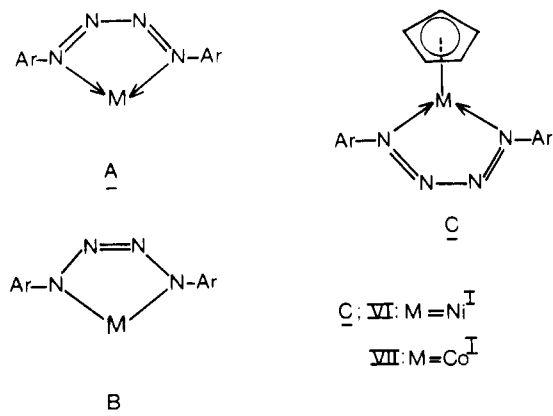
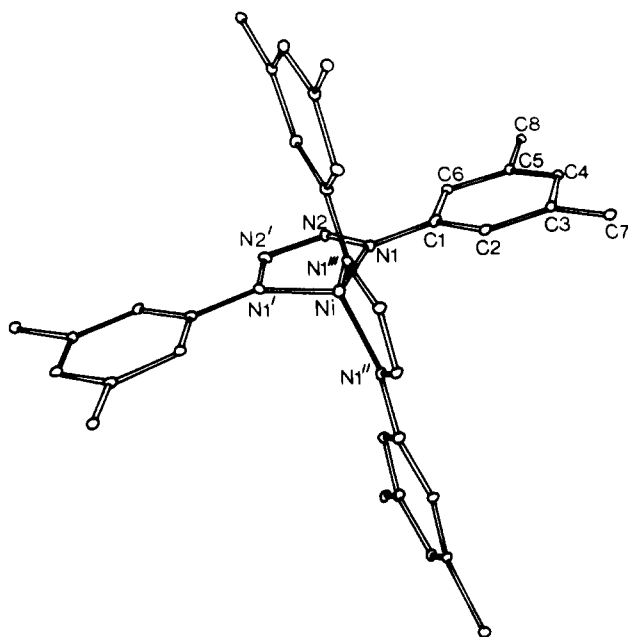**Figure 2.** The structure of $[(3,5\text{-}Me_2C_6H_3N_4C_6H_3Me_2\text{-}3,5)_2Ni]$. For relevant bond distances and angles, see ref 10.

$N_4Ar)_2]$ via both $[Ni(COD)_2]\text{-}ArN_3$ and $[CpNi^I(Ar_2N_4)]\text{-}ArN_3$ suggests that XII is also a feasible intermediate while X has been isolated as a stable compound in the case of fluorinated aryl azides.[9]

Preliminary results of reactions of $[Pt(COD)_2]$ with ArN_3 (Ar = $4\text{-}ClC_6H_4$) and with ArNCHCHNAr (Ar = $4\text{-}ClC_6H_4$ or $4\text{-}MeC_6H_4$), which afford, respectively, the novel tetraazadiene- and α-diimine-platinum complexes $[(COD)\text{-}PtAr_2N_4]$ (XIV) and $[(COD)Pt(ArNCHCHNAr)]$ (XV and XVI)[22] point to an interesting difference in the behavior of Ni and Pt, the latter, to date, yielding only the 1:1 complexes. Furthermore, both the Ni- and Pt-tetraazadiene complexes appear to have far greater stability (thermal and toward oxidation) than the corresponding α-diimine complexes.

We are currently studying the preparation and possible isolation of species of type IX–XIII to obtain deeper insight into the formation of the ArN_4Ar ligand at metal centers and the specific properties of the MN_4Ar_2 unit.

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Vrieze, *Inorg. Chim. Acta Lett.*, in press.
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(6) Anal. Found (calcd) for I ($C_{28}H_{28}N_8Ni$): C, 63.1 (62.92); H, 5.6 (5.24); O, <0.2 (0.00); N, 19.5 (20.97); Ni, 10.7 (10.86). Found (calcd) for II ($C_{28}H_{28}O_4N_8Ni$): C, 56.4 (56.12); H, 4.9 (4.68); O, 10.4 (10.69); N, 18.5 (18.71); Ni, 9.7 (9.81). Found (calcd) for III ($C_{32}H_{36}N_8Ni$): C, 64.8 (65.01); H, 6.2 (6.09); O, <0.2 (0.00); N, 18.9 (18.96); Ni, 10.2 (9.94). Characteristic absorptions in the IR spectrum of I (KBr disk, cm^{-1}): 1600 (s), 1575 (sh), 1500 (s), 1450 (m), 1175 (m), 1010 (m), 820 (vs).
(7) ^1H NMR spectra were recorded on Varian HA-100, XL-100 and T-60 spectrometers (in parts per million, at room temperature). I (in toluene-d_8): 1.50 (CH_3), 6.50 (meta), 8.40 (ortho) (J_{AB} = 8 Hz). II (in benzene-d_6): 3.40 (OCH_3), 6.80 (meta), 9.10 (ortho) (J_{AB} = 8 Hz). III (in benzene-d_6): 2.35 (CH_3), 7.05 (para), 8.50 (ortho).
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(10) From a toluene–pentane mixture tetragonal crystals of III were obtained: space group $P4_2/N$, $Z = 2$, in a unit cell with dimensions $a = b = 9.67$ (1), $c = 16.60$ (2) Å. Density obtained by flotation in $ZnCl_2$ solution: 1.198, d (calcd) 1.144 g/cm^3. Intensity measurements were carried out using Cu Kα radiation on an Enraf-Nonius CAD-4 diffractometer. A total of 1655 independent reflections was measured by θ–2θ scan; 198 of these were considered as not significant ($I < 2.5\sigma$). No absorption correction was applied. From a Patterson superposition map, based on the Ni position at $^1/_4$, $^1/_4$, $^1/_4$, all C and N atoms of the structure could be easily localized. All atoms were refined anisotropically by the x-RAY-76 block-diagonal least-squares program, using a Cruickshank weighting scheme. The H atoms were put at calculated positions and not refined. The final R index is 4.8%. Relevant bond distances (ångstroms): Ni–N(1), 1.853 (3); N(1)–N(2), 1.325 (3); N(1)–C(1), 1.426 (4); N(2)–N(2′), 1.319 (4); C(1)–C(2), 1.386 (4); C(1)–C(6), 1.394 (4); C(2)–C(3), 1.384 (4); C(3)–C(4), 1.387 (4); C(3)–C(7), 1.507 (5); C(4)–C(5), 1.386 (5); C(5)–C(8), 1.504 (5); C(5)–C(6), 1.392 (4). Relevant bond angles (degrees): N(1)–Ni–N(1′), 79.6; Ni–N(1)–N(2), 116.8; N(1)–N(2)–N(2′), 113.4; N(1)–Ni–N(1′′′), 126.2; Ni–N(1)–C(1), 128.1; N(2)–N(1)–C(1), 115.1; N(1)–C(1)–C(2), 117.2; N(1)–C(1)–C(6), 112.1; C(2)–C(1)–C(6), 120.7; C(1)–C(2)–C(3), 120.7; C(2)–C(3)–C(4), 118.2; C(2)–C(3)–C(7), 120.9; C(7)–C(3)–C(4), 120.9; C(3)–C(4)–C(5), 121.9; C(4)–C(5)–C(6), 119.5; C(4)–C(5)–C(8), 121.5; C(8)–C(5)–C(6), 118.9; C(5)–C(6)–C(1), 118.9.
(11) La Monica has reported that the reaction of $[Pt(PPh_3)_2(N_4R_2)]$ with HCl afforded RN_3, RNH_2, and *cis*-$[Pt(PPh_3)_2Cl_2]$ (R = $4\text{-}CH_3C_6H_4SO_2$): G. La Monica, P. Sandrini, F. Zingales, and S. Cenini, *J. Organomet. Chem.*, **50**, 287 (1973).
(12) Anal. Found (calcd) for V ($C_{24}H_{32}N_6Ni$): C, 62.0 (62.22); H, 6.9 (6.96); O, <0.2 (0.00); N, 18.0 (18.15); Ni, 12.7 (12.67). Yield: 17%. ^1H NMR (in acetone-d_6 in δ, ppm): 1.35 (*t*-Bu), 2.30 (CH_3tolyl), 7.05 (meta), 7.40 (ortho). IR (KBr disk, cm^{-1}): 2175 (sh), 2150 (s) (RNC terminal). V is air sensitive; in acetone the complex slowly decomposes.
(13) An optimum yield of VI was obtained after 35 min. Prolonged heating resulted in higher yields of I.
(14) VI is soluble in toluene and THF. These solutions are very sensitive to oxidation, but solid VI can be handled in air for short periods. Anal. Found (calcd) for VI ($C_{19}H_{19}N_4Ni$): C, 62.8 (63.02); H, 5.4 (5.29); O, <0.02 (0.00); N, 15.4 (15.47); Ni, 15.8 (16.21). IR (KBr disk, cm^{-1}): VI, 1500 (vs), 1410 (w), 1265 (m), 1235 (w), 1170 (m), 1095 (s), 1025 (s), 825 (s), 805 (vs); VII, 1500 (vs), 1415 (w), 1270 (m), 1230 (m), 1170 (m), 1105 (s), 1010 (s), 850 (sh), 820 (vs).
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(16) ESR spectra of VI in THF–toluene glass at -196 °C showed an orthorhombic signal with $g_1 = 1.97$, $g_2 = 2.01$, and $g_3 = 2.08$. g_2 shows a superhyperfine splitting of five equidistant lines with ~1:2:3:2:1 intensity, suggesting the presence of two magnetically equivalent N atoms ($a_N = 12$ G).
(17) VII was isolated in 11% yield from the reaction of $CoCp_2$ with ArN_3 in boiling toluene. ^1H NMR (acetone-d_6 in δ, ppm): 2.40 (CH_3), 5.00 (C_5H_5), 7.25 (meta), 7.90 (ortho) (J_{AB} = 8 Hz).
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(22) Anal. Found (calcd) for XVI ($C_{24}H_{28}N_2Pt$): C, 52.8 (53.42); H, 5.3 (5.23); O, <0.2 (0.00); N, 5.2 (5.19); Pt, 35.9 (36.16). Characteristic absorptions in the IR spectra (KBr disk, cm^{-1}): XV, 1620 (s), 1580 (s), 1480 (vs), 1365 (s), 1265 (vs), 1085 (sh), 1080 (s), 1005 (s), 880 (s), 830 (s); XVI, 1630 (s), 1600 (s), 1505 (vs), 1375 (m), 1270 (s), 890 (m), 885 (m), 820 (s); XIV, 1585 (m), 1480 (s), 1275 (s), 1080 (m), 1005 (s), 960 (m), 825 (s). Yields: XIV, 34%; XV, 34%; XVI, 34%. XIV is stable in air and soluble in CH_2Cl_2, $CHCl_3$, and THF. Solid XV and XVI are stable in air for short periods. They are soluble in toluene, but the solution decomposes very rapidly in air.
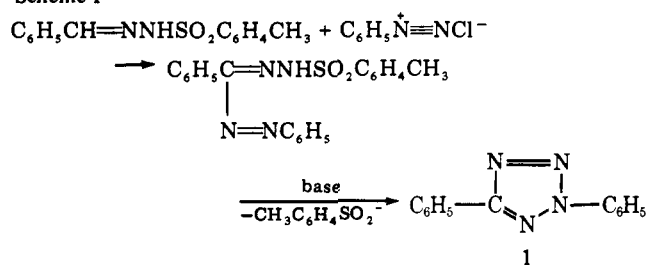
(23) (a) Anorganisch Chemisch Laboratorium; (b) Laboratorium voor Kristallo-grafie.

Peter Overbosch,[23a] Gerard van Koten,* [23a] Ok Overbeek[23b]

Anorganisch Chemisch Laboratorium and
Laboratorium voor Kristallografie
University of Amsterdam, J. H. van't Hoff Instituut
Nieuwe Achtergracht 166
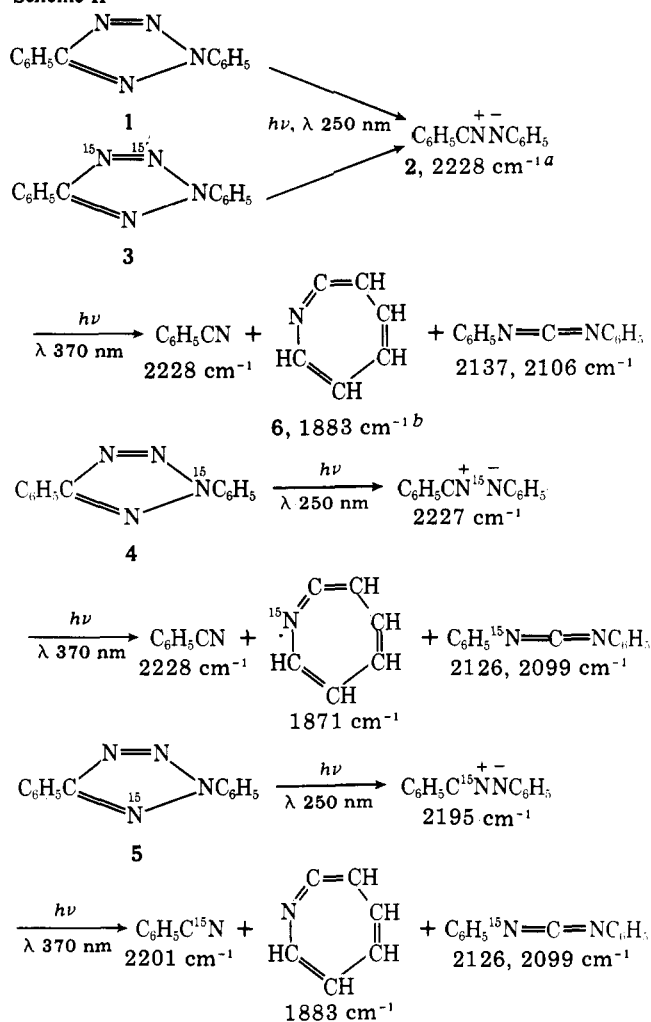*1018 WV Amsterdam, The Netherlands*
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Nitrilimines

Sir:

Nitrilimines were first prepared by Huisgen and co-workers[1] by thermal decomposition of 2,5-disubstituted tetrazoles and by base-induced elimination of hydrogen halide from hydrazonoyl halides. Their formation was demonstrated by in situ addition to alkynes, alkenes, and nitriles. The synthetic usefulness of the addition reactions of nitrilimines has since then been described in numerous papers including recently reported examples of intramolecular 1,1- and 1,3-cycloaddition reactions[2,3] and intramolecular ring closure.[4] Irradiation of sydnones[5] and tetrazoles[6] investigated in great detail by Schmid and co-workers[7] also affords nitrilimines. However, in all cases the formation of these compounds has been demonstrated only by characteristic reactions. We now report the first preparation of nitrilimines under conditions where they are stable and can be spectrally characterized.

Irradiation (λ 250 nm) of 2,5-diphenyltetrazole (**1**) in EPA (ether–isopentane–ethanol, 5:5:2) or poly(vinyl chloride) (PVC)[8] at 85 K or PVC at 10 K gives, by loss of the N(3)–N(4) atoms (Scheme I), a thermally unstable product with a strong UV absorption at 377 nm (PVC, 85 K, Figure 1). Schmid et al.[9] recently reported a similar observation with the same substrate under similar conditions [2,2-dimethylbutane-pentane, 8:3 (DMBP), 85 K]. While monitoring the formation of products by IR spectroscopy in PVC at 85 K we observed the appearance of a band at 2228 cm^{-1} (Figure 2) which, in addition to a weak signal at 2137 cm^{-1}, assigned to diphenylcarbodiimide,[10] is the only new band in the region open for observation ($\sim$1500–2800 cm^{-1}). The 2228-cm^{-1} band is in the region characteristic of heterocumulenes and triple bonds ($\sim$1900–2400 cm^{-1}).[11] Among the possibilities for the substance which absorbs at 2228 cm^{-1}, benzonitrile (2228 cm^{-1})[10] can be excluded because it is thermally stable. Phenyl isocyanide (2125 cm^{-1}, CCl$_4$),[12] diphenyldiazomethane (2041 cm^{-1}, CCl$_4$),[13] and diphenylcyanamide (2223 cm^{-1})[10] can also be excluded because of their spectral properties as well as thermal stability, which leaves diphenylnitrilimine (**2**) and *N*-isocyanodiphenylamine for further consideration. The last compound is apparently unknown, but the corresponding dialkyl derivatives give rise to absorption bands at $\sim$2100 cm^{-1}.[14] Since substitution with aryl groups is expected to give rise to absorption at lower wavenumbers, we exclude this type of compound and assign the structure of the new product to diphenylnitrilimine (**2**). Confirmation of this assignment is obtained from the results of irradiating the three differently labeled [^{15}N]-2,5-diphenyltetrazoles (**3–5**) shown in Scheme II. These were obtained by unequivocal syntheses[15] (Scheme I) from 1,2-di-^{15}N-labeled hydrazine (52.1%), ^{15}N-labeled aniline (95%), and ^{15}N-labeled sodium nitrite (95%), respectively.

Irradiation (λ 250 nm) of **1** as well as **3** gives rise to the same product demonstrating loss of the N(3)–N(4) nitrogens, whereas irradiation of either **4** or **5** gives products that retain ^{15}N. Continued irradiation (λ 370 nm) of diphenylnitrilimine (**2**, 2228 cm^{-1}) leads to benzonitrile (2228 cm^{-1}) and a

Scheme I

Scheme II

[a] The band at 2228 cm^{-1} disappears on heating to $\sim$230–240 K.
[b] The band at 1883 cm^{-1} disappears on heating to $\sim$160–170 K.

product absorbing at 1883 cm^{-1} (Figure 3). Although heating of **2** causes complete loss of the 2228-cm^{-1} band, irradiation of **2** brings about partial disappearance only. After the photochemical change, no further decrease in the intensity of the band is observed on heating, in agreement with the assignment of the band to benzonitrile. Upon irradiation of the nitrilimine generated from **4**, unlabeled benzonitrile is formed and the absorption formerly at 1883 cm^{-1} is shifted to 1871 cm^{-1} because of the presence of ^{15}N in the corresponding compound. On the other hand, irradiation of the nitrilimine from **5** gives rise to labeled benzonitrile (2201 cm^{-1}) and absorption at 1883 cm^{-1} as before. We identify the compound responsible for the absorption at 1883 cm^{-1} as 1-aza-1,2,4,6-cycloheptatetraene (**6**) (Scheme II), which has recently been observed by Chapman and co-workers as a product of irradiation of phenyl azide in an Ar matrix at 8 K.[16] Although this compound absorbs at 1895 cm^{-1} in an Ar matrix,[16] irradiation of phenyl azide in