rubidium is surrounded by three others in a shell of radius 4.0 Å < r < 4.5 Å: d(Rb···Rb(5 0 0 1)) = 4.03 Å, d(Rb···Rb(3 0 0 0)) = 4.32 Å, and d(Rb···Rb(7 0 1 1)) = 4.42 Å.[14] All the short distances obtained from the packings are reported in Table III along with the connecting symmetry operators to be applied on the second atom.

This very different situation of the cation short contacts with respect to the Ag^+ salt leads now to a shielding effect not selectively distributed (the short distances are now in the range 2.8–3.2 Å) over all the alkylation sites. This could be a good explanation of the nonreactivity of the rubidium salt when the solid state is implicated in the alkylation process (heterogeneous dispersion in CH_2Cl_2). Moreover, this shielding is enhanced by the aggregation of the rubidium atoms in meridian planes, which acts as an additional steric protection against the alkylating reagent.

Conclusion

The present study shows a good agreement between the packing structures of two solid salts of ambident anions of the 2-phenyl-1,3,4-oxadiazol-5(4*H*)-one and their reactivity in alkylation reaction under heterogeneous conditions: (1) In the Ag^+ salt, where a strong ion pair exists, the O(6) oxygen atom (and, to a lesser extent, the N(3) nitrogen atom) remains unprotected and thus can be alkylated with a high selectivity. (2) In the Rb^+ salt, a widely distributed shielding effect of different, symmetrically related cations, occurs; all the atoms of the anion are affected by this shielding and the anion cannot be alkylated at any position.

Thus, the steric hindrance of the cation over the rest of the molecule can be considered as the leading factor in the control of the regioselectivity observed *in heterogeneous conditions*. These results strongly suggest that the same kind of steric effect might also explain the behavior of the other alkaline salts of the 2-phenyl-1,3,4-oxadiazol-5-(4*H*)-one, which is the same as that of the rubidium salt.

Registry No. 2-Phenyl-1,3,4-oxadiazol-5(4*H*)-one silver salt, 98218-22-5; 2-phenyl-1,3,4-oxadiazol-5(4*H*)-one rubidium salt, 98218-23-6.

Supplementary Material Available: Tables containing positional parameters with anisotropic thermal u factors, distances, and angles and stereorepresentations of Figures 2 and 3 (6 pages). Structure factor tables are available from the authors. Ordering information is given on any current masthead page.

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[14] The symbolic of symmetry operations to be applied on the second atom is given in Table III.

Electrocyclization and Cyclooligomerization Reactions of 2,7-Dimethyl-2,3,5,6-octatetraene with Ni(0) and Ni(II) Complexes

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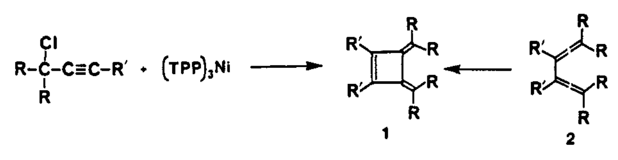
The reactions of 2,7-dimethyl-2,3,5,6-octatetraene (DMOT) with several Ni(0) and Ni(II) complexes have been investigated. The results indicate that the product(s) produced depends on the nature of the ligands attached to the nickel and the oxidation state of the nickel atom. The reaction of DMOT with tris(triphenylphosphine)nickel(0) [$(TPP)_3Ni$] quantitatively produces the cyclic trimer **3**. In contrast, the reaction of DMOT with bis(cyclooctadiene)nickel(0) [$(COD)_2Ni$] results in the electrocyclic ring closure to **4** and the formation of the cyclic dimer **5**. The reaction of DMOT with a mixture of $(COD)_2Ni$ and (COD)(TPP)Ni results in the formation of a mixture of **3** and **5**. The electrocyclic ring closure of DMOT to **4** is catalyzed by bis(triphenylphosphine)nickel dibromide, but not by bis(triethylphosphine)nickel dibromide. A general mechanism is proposed for the reactions of DMOT with the Ni(0) complexes.

In an attempt to prepare allenylnickel complexes by the oxidative insertion of a Ni(0) complex with substituted propargyl chlorides, we discovered an unusually facile formation of 3,4-bis(alkylidene)cyclobutenes **1**.[1] A reasonable mechanism was thought to involve the formation of intermediate substituted 1,2,4,5-tetraenes **2**. Prior studies in our[2] and other laboratories[3] had shown that the electrocyclic ring closure of **2** to **1** occurred thermally, however, under much more vigorous conditions than those employed for the formation of **1** in the reactions of the Ni(0) complexes with the substituted propargyl chlorides.



This suggested that the conversion of **2** to **1** was catalyzed by some Ni species present in the reaction mixture. In a continuation of our studies of the reactions of substituted allenes with Ni(0) complexes[4] we have now studied the reactions of 2,7-dimethyl-2,3,5,6-octatetraene (DMOT) with Ni(0) and Ni(II) complexes.

Results and Discussion

The reaction of DMOT with $(TPP)_3Ni$ at room temperature in toluene-d_8 results in the rapid (<3 h) and quantitative (by NMR) formation of the cyclic trimer **3**. The ^1H and ^{13}C NMR spectra suggested that the product was a trimer of DMOT; although the mass spectrum showed only a very weak peak at m/e 402, the most intense peak in the spectrum appearing at m/e 268 (a dimeric structure of DMOT). The vinyl hydrogen region of the ^1H NMR spectrum of **3** showed one set of AB doublets,

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[1] Pasto, D. J.; Mitra, D. K. *J. Org. Chem.* **1982**, *47*, 1381.

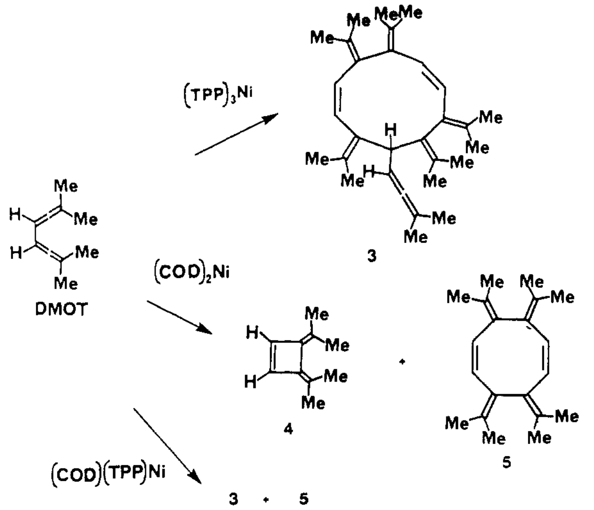
[2] Pasto, D. J.; Waterhouse, A., unpublished observations.

[3] Skattebol, L.; Solomon, S. *J. Am. Chem. Soc.* **1965**, *87*, 4506.

[4] (a) Pasto, D. J.; Huang, N.-Z. *Organometallics* **1985**, *4*, 1386. (b) *J. Am. Chem. Soc.* **1985**, *107*, 3160.

0022-3263/85/1950-4465$01.50/0

a singlet for two hydrogens, and a double septet, the septet coupling of 2.62 Hz suggesting the presence of a 3,3-dimethylallenyl group. The methyl groups of the 3,3-dimethylallenyl group appeared as two doublets, indicating the presence of a chiral center in the molecule. The presence of a single allene chromophore in **3** was confirmed by the appearance of two resonances in the ^{13}C NMR spectrum at δ 90.9 and 95.4 characteristic of the terminal allene carbon atoms.[5] In addition to the two allenyl methyl groups, the ^1H and ^{13}C NMR spectra indicated the presence of ten other vinyl methyls. The UV spectrum of **3** displayed a maximum at 275 nm, suggesting the presence of a polysubstituted, conjugated triene chromophore. Overall, the spectral data are only consistent with structure **3** for the cyclic trimer.



The addition of DMOT at low temperature (<−70 °C) to a solution of $(TPP)_3Ni$ in toluene-d_8 did not indicate the formation of any π or σ complexes, the resonances of DMOT retaining their characteristic positions and multiplicities. On raising the temperature of the sample to 20 °C the peaks of DMOT disappeared with the concomitant appearance of the peaks of **3**. *No other peaks were detected characteristic of intermediate π or σ complexes.* Attempts to intercept σ complexes by carbonylation proved futile.[6]

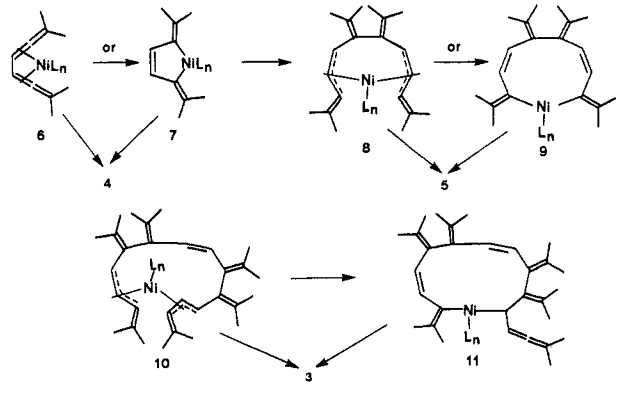
The reaction DMOT with bis(cyclooctadiene)nickel(0) resulted in the formation of a mixture of **4** and the cyclic dimer **5**. The symmetric nature of **5** was indicated by the presence of a single vinyl hydrogen resonance and two vinyl methyl resonances and its dimeric nature by its mass spectrum. During the reaction of DMOT with $(COD)_2Ni$ a fine black precipitate was slowly formed, presumably finely divided metallic nickel. Control reactions indicated that this precipitate was not active as a catalyst in the transformation of DMOT to either **4** or **5**. The slow precipitation of Ni precluded carrying out NMR experiments, only very broad lined spectra being obtained.

In the presence of the mixed ligand complex (COD)(TPP)Ni(0), which also undoubtedly contains some $(TPP)_3Ni(0)$, DMOT reacts to produce a mixture of the dimer **5** and trimer **3**. The reacting solution was monitored by NMR, however no peaks were obtained for any possible intermediates formed during the reaction. Attempted carbonylation did not produce any ketonic products.

The thermal ring closure of DMOT occurs rather slowly at 70 °C.[7] In the presence of 10 mol % of $(TPP)_2NiBr_2$, the conversion of DMOT to **4** is markedly accelerated. The presence of tris(triethylphosphine)nickel dibromide had no catalytic effect on the ring closure of DMOT.

Discussion

The results derived from the reactions of DMOT with the Ni(0) complexes show that the type of product formed depends on the nature of the ligands present in the complex. In the presence of $(COD)_2Ni$ simple ring closure and cyclodimerization is observed. This behavior is quite different than that observed in the reaction of dimethylallene (DMA) with $(COD)_2Ni$ in which linear oligomerization and polymerization is observed, apparently induced by an electron transfer from the nickel to the DMA.[4a] The inability to observe or trap any intermediate in the conversion of DMOT to **4** makes it impossible to define the type of complex(es) involved in the reactions. Two possibilities exist for the formation of **4**; direct cyclization in the π-complex **6**, or reductive elimination in the σ-complex **7**. Nickelacyclopentane σ complexes have been characterized as intermediates in the reactions of substituted allenes with $(TPP)_3Ni$, although reductive elimination to form four-membered ring systems was not observed.[4] In the presence of TPP, **4** is not formed, indicating that the presence of TPP must stabilize **6** or **7** toward the elimination of **4**. In the reaction of DMOT with $(COD)_2Ni$ the further reaction of the monoDMOT complex (**6** or **7**) with DMOT produces a bis(DMOT)nickel complex which reductively eliminates the dimer **5**. Three possibilities exist for the structure of the bis(DMOT) complex; a bis(π-allyl) complex **8**,[8] the σ-complex **9**, and a mixed π,σ complex. In the presence of only TPP as a ligand on nickel the bis(DMOT) complex is stabilized relative to reductive elimination and reacts further to produce a tris(DMOT) complex which undergoes reductive elimination to form the cyclic trimer **3**. As with the bis(DMOT) complex, three structures are possible for the tris(DMOT) complex, the bis(π-allyl) complex **10**, the σ-complex **11**, and a mixed π,σ complex. The reductive elimination within **10** (or **11**) to produce the 10-membered ring product **5** instead of a 12-



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[5] The central allenyl carbon atom could not be unambiguously assigned in the ^{13}C NMR spectrum because of the long relaxation time of these types of carbon atoms. The relatively small quantities of **3** available and the chemical reactivity of **3** did not allow for more extensive NMR studies to be carried out.

[6] In the reactions of $(TPP)_3Ni$ with substituted allenes the intermediacy of σ complexes was readily demonstrated by the isolation of cyclic ketones on treament with carbon monoxide (see ref 4).

[7] The results of a kinetic study on this reaction will be published separately.

[8] Bis(π-allyl) complexes have been observed by low-temperature NMR in the cyclooligomerization of dienes: Büssemeier, B.; Jolly, P. W.; Wilke, G. *J. Am. Chem. Soc.* **1974**, *96*, 4726. Wilke, G.; Bogdanovic, B.; Hardt, P.; Heimback, P.; Keiss, W.; Kröner, M.; Oberkirch, W.; Tanaka, K.; Steinrücke, E.; Walter, D.; Zimmerman, H. *Angew. Chem.* **1966**, *78*, 157. Wilke, G.; Bogdanovic, B. *Angew. Chem.* **1961**, *73*, 756. Wilke, G. *Angew. Chem.* **1963**, *75*, 10. Henc, B.; Jolly, P. W.; Salz, R.; Wilke, G.; Benn, R.; Hoffmann, E. G.; Mynott, R.; Schroth, G.; Seevogel, K.; Sekutowski, J. C.; Kruger, C. *J. Organomet. Chem.* **1980**, *191*, 425.

membered ring triene would appear to be controlled by steric factors. The tris(DMOT) complex does not react further with DMOT.

The conversion of DMOT to 4 is catalyzed by Ni(II) complexes. It has been previously observed that the electrocyclic ring closure of 1,2,4,5-hexatetraene is catalyzed by cuprous chloride in liquid ammonia.[9] In the present case the ring closure of DMOT is catalyzed by the triphenylphosphine complex of nickel bromide but not by the triethylphosphine complex. As triethylphosphine is a more strongly binding ligand to nickel, this would suggest that dissociation of a phosphine ligand from the nickel bromide complex is required. The further details of the mechanism cannot be deduced with the available information.

Experimental Section

Reaction of 2,7-Dimethyl-2,3,5,6-octatetraene (DMOT) with Tris(triphenylphosphine)nickel(0) [$(TPP)_3Ni$]. To 0.014 g (0.05 mmol) of $(COD)_2Ni$ in 1.0 mL of toluene-d_8 under an argon atmosphere in an NMR tube equipped with a septum screw cap was added 0.04 g (0.15 mmol) of TPP. The NMR spectrum of the resulting solution showed resonances only for free COD. To this solution was added 0.07 g (0.5 mmol) of DMOT dissolved in 0.2 mL of toluene-d_8.[10] The NMR spectrum recorded immediately showed somewhat broadened resonances, which quickly returned to normal width. The NMR spectrum of the reaction solution showed only the resonances of DMOT and 3. After 3 h the NMR spectrum indicated a quantitative conversion of DMOT to 3. The solvent was removed under reduced pressure, and the residue was subjected to rotating disk chromatography using a 1 mm thick silica gel plate. Elution with pentane gave 0.060 g (86%) of an air-sensitive, viscous, pale yellow oil: ^1H NMR ($CDCl_3$) δ 1.53 (s, 6 H), 1.55 (s, 3 H), 1.58 (d, J = 2.62 Hz, 3 H), 1.59 (d, J = 2.62 Hz, 3 H), 1.66 (s, 3 H), 1.70 (s, 6 H), 1.78 (s, 3 H), 1.79 (s, 3 H), 1.83 (s, 6 H), 4.39 (d, J = 6.85 Hz, 1 H), 4.77 (dh, J = 6.85, 2.62 Hz, 1 H), 6.12 (s, 2 H), 6.19 (d, J = 10.11 Hz, 1 H), 6.36 (d, J = 10.11 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 19.6, 20.2, 20.3, 20.5, 20.7 (2 C), 21.1 (2 C), 22.8 (2 C), 23.1 (2 C), 41.6, 90.9, 95.4, 121.5, 124.4, 125.0, 127.0 (2 C), 127.9, 129.6, 129.8, 130.2, 132.1, 132.2, 132.3, 132.6, 132.8 [under non-proton decoupling the following multiplets were observed, δ 41.6 (d, J = 125 Hz), 90.9 (d, J = 166 Hz), 121.5 (d, J = 156.7 Hz), 125.0 (d, J = 160.4 Hz), 127.0 (d, J = 157.0 Hz, 2 C)]; UV (95% ethanol) λ_{max} 275 (log ε 3.34); MS (very low intensity peak at m/e 402, major peak at m/e 268), exact mass calcd for $C_{20}H_{28}$ 268.219, found 268.219.

Low-Temperature Monitoring of the Reaction of DMOT with $(TPP)_3Ni$. A solution of $(TPP)_3Ni$ in toluene-d_8 was prepared as described above, and DMOT was added at <−70 °C. At −70 °C the NMR spectrum indicated that no reaction had occurred. The temperature of the reaction mixture was slowly raised and the NMR spectrum was recorded periodically. At approximately 10 °C the conversion of DMOT to 3 was observed. Only peaks characteristic of DMOT and 3 were present in the spectrum.

Treatment of a DMOT–$(TPP)_3Ni$ Reaction Mixture with Carbon Monoxide. To 0.16 of $(TPP)_3Ni$ (prepared as described above) in 5 mL of benzene at 25 °C was added 0.32 mmol of DMOT. After 5 min, carbon monoxide was bubbled through the reaction mixture for 0.5 h. The solvent was removed under reduced pressure. The IR spectrum of the residue did not contain a peak in the $\nu_{C=O}$ region.

Reaction of DMOT with Bis(1,5-cyclooctadiene)nickel(0) [$(COD)_2Ni$]. To 0.093 g (0.34 mmol) of $(COD)_2Ni$ in 5 mL of THF at −78 °C under an argon atmosphere was added 0.090 g (0.68 mmol) of DMOT. The temperature was slowly raised to −10 °C, during which time the solution turned red-brown in color. The NMR spectrum of the reaction solution showed only very broad peaks. The reaction mixture was allowed to stand at 25 °C for 16 h, during which time a finely divided black material precipitated. The reaction mixture was diluted with 15 mL of pentane and was filtered. The solvent was carefully removed under reduced pressure and residue was chromatographed on a 1-mm silica gel rotating disk with hexane as eluant. Three fractions were collected.

Fraction 1 (5, 30%): ^1H NMR ($CDCl_3$) δ 1.28 (s, 12 H), 1.47 (s, 12 H), 6.05 (s, 4 H); UV (95% ethanol) λ_{max} 263 nm (log ε 3.46); MS, exact mass calcd for $C_{20}H_{28}$ 268.219, found 268.219.

Fraction 2[1] (4, 17% as a very air-sensitive liquid): ^1H NMR ($CDCl_3$) δ 1.51 (s, 6 H), 1.70 (s, 6 H) and 6.76 (s, 2 H); UV (95% ethanol) λ_{max} 258 nm (log ε 2.96).

Fraction 3: ^1H NMR ($CDCl_3$), very broad peaks in the high-field region suggesting a polymeric material.

Reaction of DMOT with (COD)(TPP)Ni. In an NMR tube equipped with a septum screw cap was placed 0.0194 g (0.07 mm) of $(COD)_2Ni$ under an argon atmosphere. The $(COD)_2Ni$ was dissolved in 0.5 mL of benzene-d_6, and 0.21 mmol of TPP dissolved in 0.5 mL of benzene-d_6 was added. The NMR spectrum of the resulting solution showed peaks at δ 2.28 and 5.72 for free COD and at δ 1.71, 1.96, and 4.98 for the mixed ligand complex (COD)(TPP)Ni.[11] No peaks were present at δ 2.19 and 4.42 for $(COD)_2Ni$. To this solution was added 0.019 g (0.14 mmol) of DMOT. The NMR spectrum recorded immediately indicated the complete disappearance of (COD)(TPP)Ni. After 5 min, the peaks of DMOT had disappeared, and peaks characteristic of 3 and 5 were present.

Registry No. 3, 98652-42-7; 4, 3642-14-6; 5, 98652-43-8; DMOT, 3642-20-4; $(COD)_2Ni$, 1295-35-8; $(TPP)_3Ni$, 25136-46-3; (COD)(TPP)Ni, 98652-44-9; $(TPP)_2NiBr_2$, 14126-37-5; tris(triethylphosphine)nickel dibromide, 98652-45-0.

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[9] Hopf, H.; Lenich, F. T. *Chem. Ber.* **1973**, *106*, 3461.

[10] Similar results were obtained when the COD and solvent were pumped off on a vacuum line and the residue was dissolved in toluene-d_8.

[11] Stoichiometric studies in these laboratories suggest that the mixed ligand complex possesses the formula (COD)(TPP)Ni in solution.