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PROJECT TITLE: Bimetallic Promotion of Cooperative Hydrogen Transfer and Heteroatom Removal in Coal Liquefaction

GRANT NO.: DE-FG22-88PC88930

QUARTERLY SUMMARY

OBJECTIVES: The ultimate objective of this research is to uncover new catalytic processes for the liquefaction of coal and for upgrading coal-derived fuels by removing undesirable organosulfur, organonitrogen and organooxygen constituents. Basic to both the liquefaction of coal and the purification of coal liquids is the transfer of hydrogen from such sources as dihydrogen, metal hydrides or partially reduced aromatic hydrocarbons to the extensive aromatic rings in coal itself or to aromatic sulfides, amines or ethers. Accordingly, this study is exploring how such crucial hydrogen-transfer processes might be catalyzed by soluble, low-valent transition metal complexes and/or Lewis acids under moderate conditions of temperature and pressure. By learning the mechanism whereby H_2, metal hydrides or partially hydrogenated aromatics do transfer hydrogen to model aromatic compounds, with the aid of homogeneous, bimetallic catalysts, we hope to identify new methods for producing superior fuels from coal.

WORK: During the twelfth quarter of this 40-month grant (with a four-month, no-cost extension) the following aspects of our research program received attention: 1) continuation of studies aimed at assessing the synergistic effect of nickel(0) complexes, combined with organoaluminum Lewis acids, in promoting hydrogen transfer and heteroatom removal in organic substrates; 2) further investigation of the effect of ligands in activating nickel(0) complexes for the rupture of carbon-heteroatom linkages (C-E, where E = nitrogen, sulfur, halogen and oxygen); and 3) attempts to detect, trap and synthesize independently the nickel intermediates responsible for hydrogen transfer and heteroatom removal in the foregoing processes.

ACHIEVEMENTS: Three noteworthy observations concerning our catalyzed hydrogen-transfer and desulfurization reactions have been made during the last quarter: 1) the synergistic effect of i-Bu_3Al and $(Cod)_2Ni$ on the hydrogen transfer between 9,10-dihydroanthracene and diphenylacetylene has been found to be promoted by visible light; 2) the desulfurization of dibenzothiophene by $MeAlCl_2$ and hydrogen donors has been shown to involve an Umpolung of the methyl group; and 3) the bright red complex formed from $(Cod)_2Ni$ and benzonitrile is thought to be 3-phenylnickelaazirine and to be the key intermediate in the dimerization and trimerization reactions.

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QUARTERLY TECHNICAL PROGRESS REPORT

October 1, 1991

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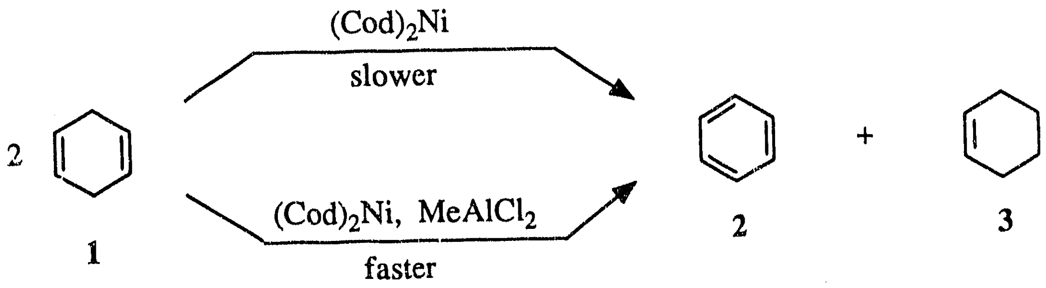
PERIOD OF PERFORMANCE: 06/01/91 - 08/31/91

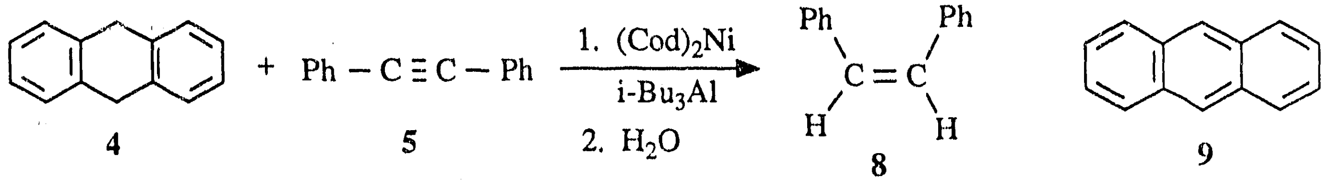
<u>OBJECTIVES</u>: The ultimate objective of this research is to uncover new catalytic processes for the liquefaction of coal and for upgrading coal-derived fuels by removing undesirable organosulfur, organonitrogen and organooxygen constituents. Basic to both the liquefaction of coal and the purification of coal liquids is the transfer of hydrogen from such sources as dihydrogen, metal hydrides or partially reduced aromatic hydrocarbons to the extensive aromatic rings in coal itself or to aromatic sulfides, amines or ethers. Accordingly, this study is exploring how such crucial hydrogen-transfer processes might be catalyzed by soluble, low-valent transition metal complexes and/or Lewis acids under moderate conditions of temperature and pressure. By learning the mechanism whereby H_2, metal hydrides or partially hydrogenated aromatics do transfer hydrogen to model aromatic compounds, with the aid of homogeneous, bimetallic catalysts, we hope to identify new methods for producing superior fuels from coal.

<u>PRESENT WORK AND ACCOMPLISHMENTS</u>: <u>Synergistic Hydrogen Transfer</u>. During the twelfth quarter of this 3.33-year grant, we have continued studies on the possible synergistic action of nickel(0) complexes and organoaluminum Lewis acids on hydrogen transfer processes. A clue as to the existence of such synergism was that the nickel(0)-catalytic disproportionation of 1,4-cyclohexadiene (**1**) into benzene (**2**) and cyclohexene (**3**) was found to be accelerated by the presence of methylaluminum dichloride (eq. 1):



(1)

Similar to this <u>homomolecular</u> hydrogen transfer, we have now observed an instance of <u>heteromolecular</u> hydrogen transfer. For example, when a 1:1 molar mixture of 9,10-dihydroanthracene (**4**) and diphenylacetylene (**5**) is treated, separately, with one molar equivalent of either bis(1,5-cyclooctadiene)nickel (**6**) or triisobutylaluminum (**7**) in toluene at 25°C, hydrolytic workup after 3 to 5 days yields 5-10% of cis-stilbene (**8**). When a 1 : 1 : 1 : 1 mixture of **4**, **5**, **6** and **7** is allowed to react for 3 days, a complete conversion of **4** and **5** into anthracene (**9**) and cis-stilbene (**8**) was realized (eq. 2). In the unhydrolyzed reaction mixture (step 1), both isobutane and isobutene were detected by ^{1}H NMR spectroscopy.



(2)

Unexpectedly, when the ratio of triisobutylaluminum used in such a hydrogen transfer reaction was reduced to 0.33 and the ratio of **4**, **5** and **6** was maintained at 1 : 1 : 1, the diphenylacetylene was still completely converted to cis-stilbene (**8**) but the 9,10-dihydroanthracene (4) was unchanged. In this case, no anthracene was formed and thus **4** did not transfer hydrogen to **5**. Moreover, in the unhydrolyzed reaction mixture only isobutene was detected by ^{1}H NMR spectroscopy.

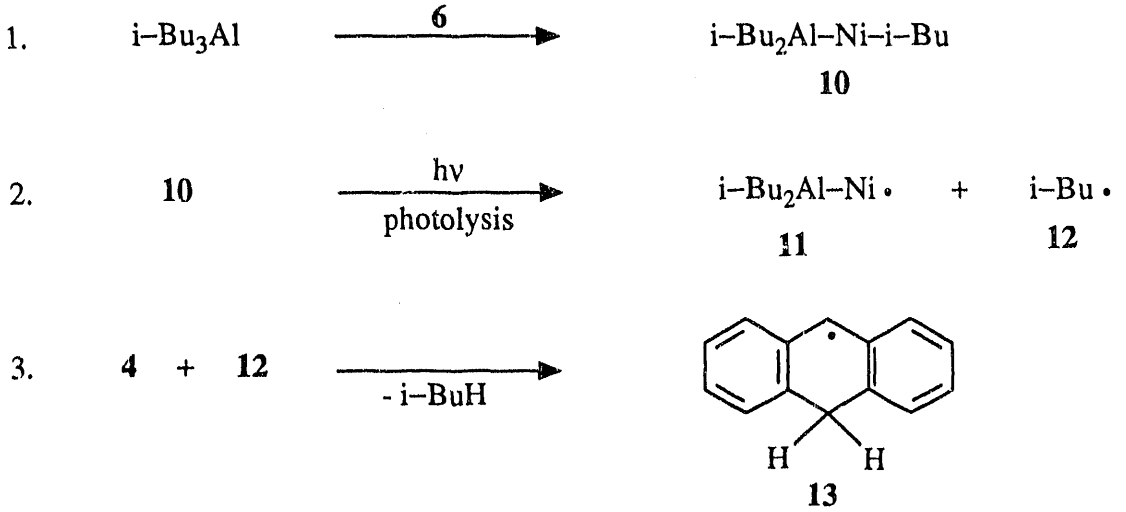
In further probing the nature of this synergistic hydrogen transfer, the following changes were made in the experimental conditions:

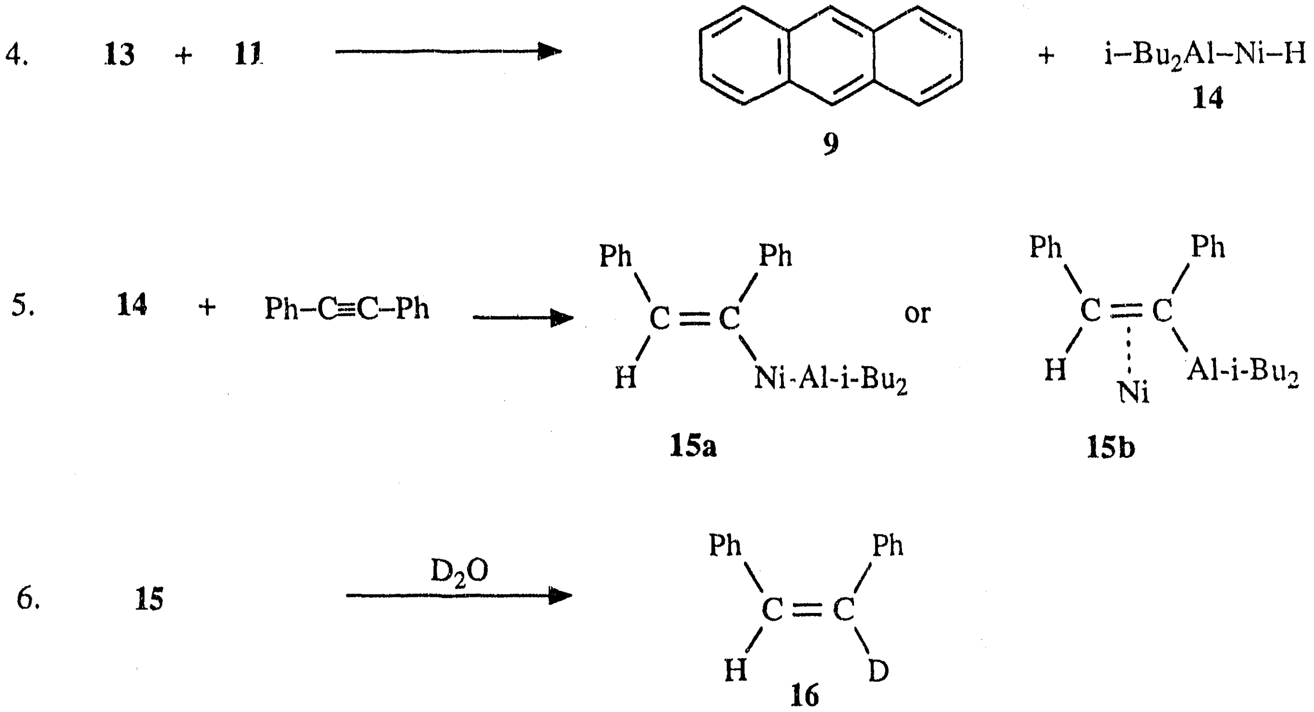
1. A 1 : 1 : 1 : 1 mixture of **4**, **5**, **6** and **7** in toluene was allowed to react for 4 days at 25°C with the complete exclusion of visible light. In contrast with the complete conversion obtained in the presence of visible light, only 30% of the 9,10-dihydroanthracene was converted to anthracene but 100% of the diphenylacetylene was converted to cis-stilbene, after hydrolytic workup. Therefore, the involvement of the 9,10-dihydroanthracene is clearly promoted by visible light;

2. A 1 : 0.05 : 1 mixture of **5**, **6** and **7** in toluene was allowed to react for 2 days at 25°C with exposure to room light. Upon hydrolysis, the diphenylacetylene was completely converted to cis-stilbene. Therefore, the transfer of the Al-H bonds from **6** to **5** is catalyzed by nickel(0).

For the case of catalysis of hydrogen transfer by a 1 : 1 stoichiometric mixture of i-Bu$_3$Al and (c-C$_8$H$_{12}$)$_2$Ni with the involvement of the 9,10-dihydroanthrene and the formation of isobutane, the following reaction Scheme I is proposed.

Scheme I

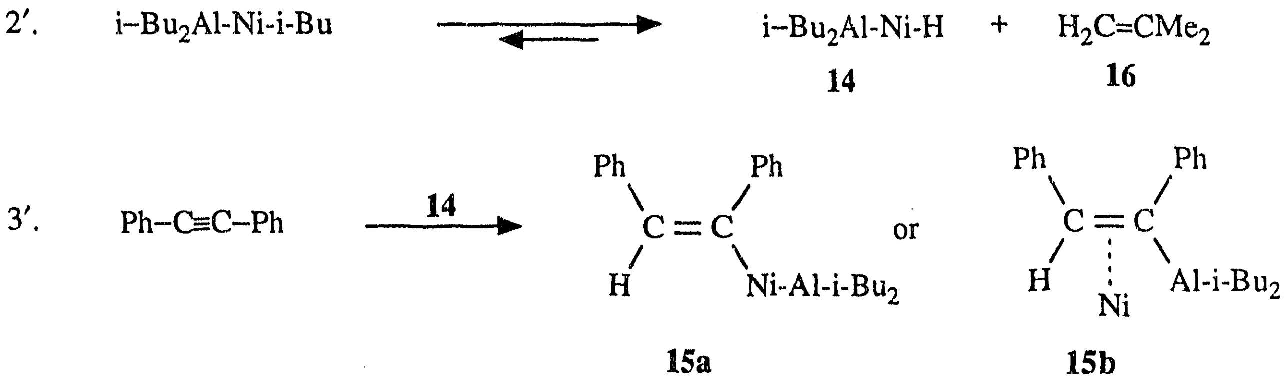




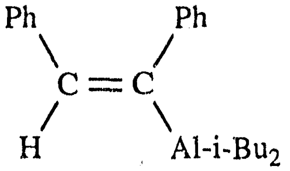
Also this mechanism would require a <u>cis</u>-stilbenylmetallic derivative be present before hydrolysis (**15** in step 5) and that α-deuterio-<u>cis</u>-stilbene be thereafter formed if D_2O is added. In fact, work-up with D_2O did produce **16** (step 6).

For the case of catalysis by a 0.05 : 1.0 ratio of **6** : **7** <u>without</u> the involvement of 9,10-dihydroanthracene and with the formation of isobutene, an alternative mode of decomposition for intermediate **10** (step 2) is suggested in Scheme II:

Scheme II



4′. **15b** $\rightleftharpoons$


$$\mathrm{Ph(H)C{=}C(Ph)Al\text{-}i\text{-}Bu_2}$$

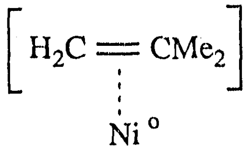
+ Ni^o

(reenters at step 1 to establish a catalytic cycle.)

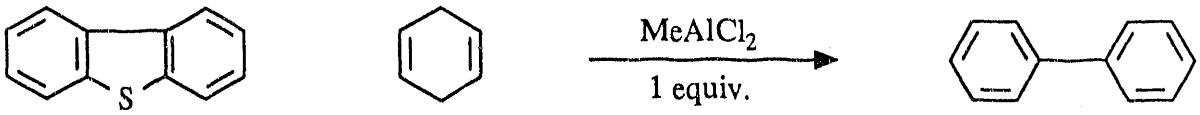
Possibly step 2′ becomes more important than step 2 in Scheme I for two reasons: 1) in the presence of excess $(c\text{-}C_8H_{12})_2Ni$ over $i\text{-}Bu_3Al$ (1.0 : 0.33), Ni(0) scavenges free radicals (step 2) and thus prevents their attack on **4** (step 3) (eq. 3):

$$\underset{\mathbf{12}}{2\ i\text{–}Bu\ \bullet} + \underset{\mathbf{6}}{Ni^o} \longrightarrow i\text{–}Bu_2Ni \qquad (3)$$

and 2) nickel(0) in excess could complex with isobutene in step 2′ and drive equilibrium to the right (eq. 4):

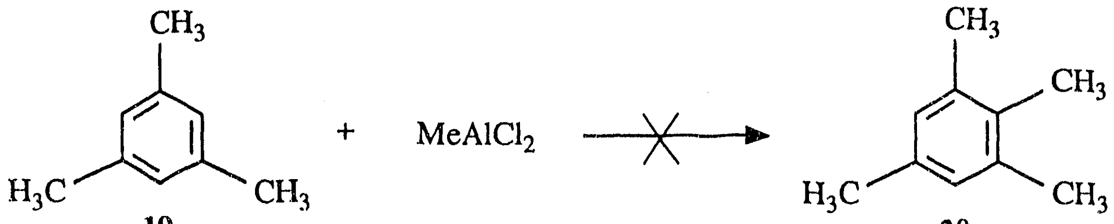

$$\underset{\mathbf{10}}{i\text{–}Bu_2Al\text{-}Ni\text{-}i\text{-}Bu} \rightleftharpoons \underset{\mathbf{14}}{i\text{–}Bu_2Al\text{-}Ni\text{-}H} + \underset{\mathbf{16}}{H_2C{=}CMe_2} \rightleftharpoons \left[\underset{\underset{Ni^{o}}{\vdots}}{H_2C = CMe_2}\right]_n \qquad (4)$$

<u>Desulfurization of Dibenzothiophene by Lewis Acids and Hydrogen Donors</u>. During this project we have observed a remarkably facile desulfurization of dibenzothiophene (**16**) (eq. 5):



16 **17** MeAlCl$_2$ 1 equiv. 25°C **18** (5)

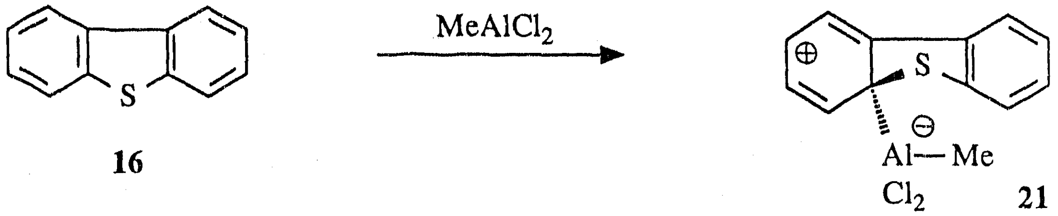
Although the maximum yield of biphenyl thus far obtained is 25% and both the fate of the sulfur and the nature of by-product are as yet unknown, a further interesting observation has now been made. When **16** is heated with mesitylene (**19**) in the presence of $MeAlCl_2$ but without **17**, the mesitylene is converted into 1,2,3,5-tetramethylbenzene (**20**). This result suggests that mesitylene has now undergone a Friedel-Crafts methylation catalyzed by the Lewis acid, $MeAlCl_2$. But in a separate experiment it was shown that $MeAlCl_2$alone was unable to transform **19** into **20** (eq. 6):



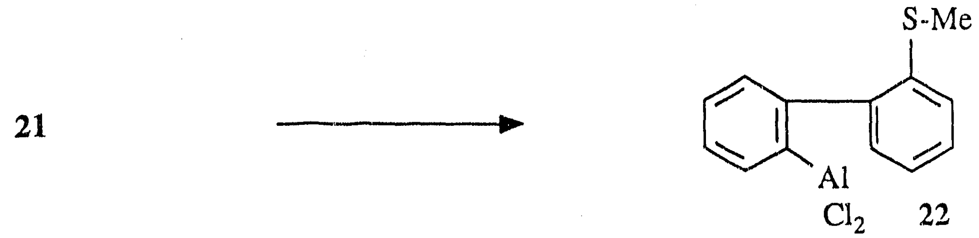
19 **20** (6)

Only when **16** was <u>also</u> present did the conversion depicted in eq. 6 occur.

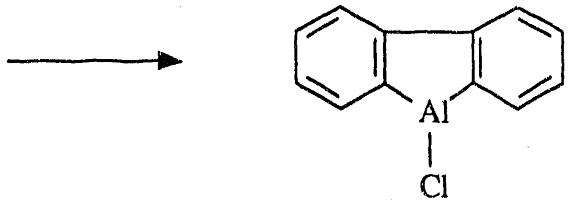
Now the only ready source of the methyl group needed to form **20** is the methylaluminum dichloride. However, its polarity, $\overset{\delta-}{CH_3}\text{-}\overset{\delta+}{AlCl_2}$, is not that required for a Friedel-Crafts methylation where a positively polarized methyl group is needed, as in $\overset{\delta-}{CH_3}\text{-}\overset{\delta+}{Cl}$. What must occur then in the desulfurization of **16** by $MeAlCl_2$ is the reversal of polarization of the methyl group (Umpolung in German) as the carbon-sulfur bond is cleaved. Based upon these observations, we propose the following desulfurization mechanism (eqs. 7 - 9):



16 **21** (7)



22 (8)



+ Me-S-Cl

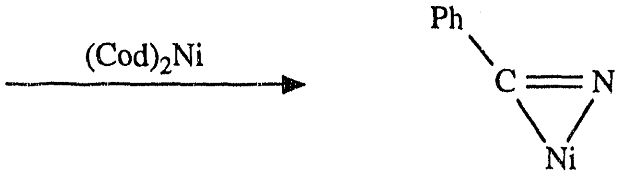
23 (9)

The methanesulfenyl chloride (**23**) formed in eq. 9 would have the appropriately polarized methyl group, $\overset{\delta-}{CH_3}\text{-}\overset{\delta+}{SCl}$ to function as a Friedel-Crafts alkylating agent toward mesitylene.

<u>Oligomerization of Benzonitrile</u>. The initial interaction of $(Cod)_2Ni$ with benzonitrile (**24**) leads to the formation of a bright-red 1 : 1 adduct (**25**), whose hydrolyzes yields benzaldehyde. In the absence of X-ray crystal data, we conclude therefore that **25** is 3-phenylnickelaazirine (eq. 10):

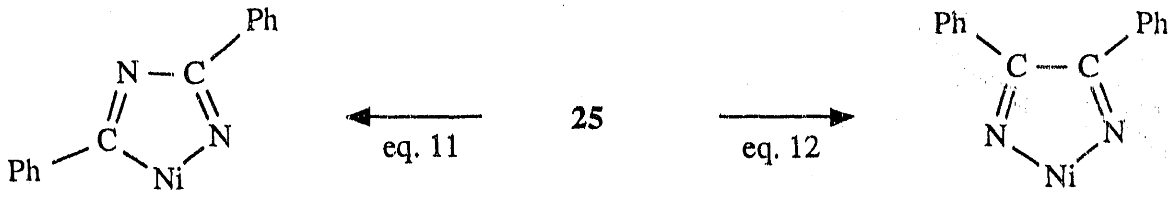
Ph-C≡N

24



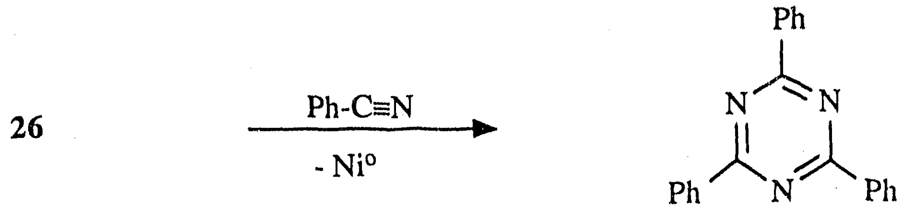
25 (10)

With such an intermediate in hand, the oligomerization of **24** into dimers and trimers can be readily visualized as ensuing from further insertions of **24** units into the C-Ni bond of **25** (eqs. 11-12):



26 **27**

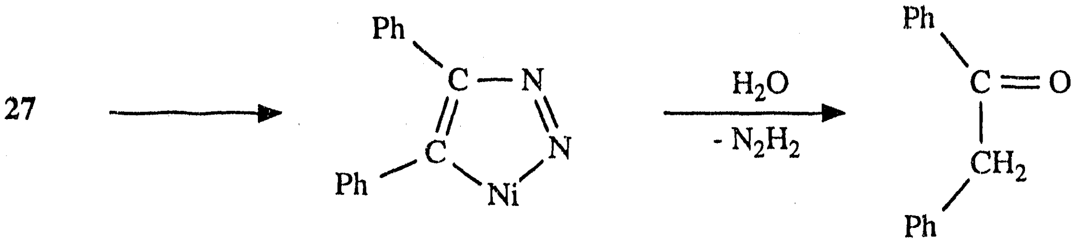
Intermediate **26**, upon further insertion of **24** and elimination of Ni°, could yield the observed triazine **28** (eq. 13):



28

(13)

Similarly, intermediate **27** could isomerize and then hydrolyze and eliminate dimine to the observed ketone **29** (eq. 14):



29

(14)

<u>PLANS FOR THE NEXT QUARTER</u>: First, we shall finish our studies on the synergistic catalysis of hydrogen transfer and of desulfurization as promoted by combinations of Lewis acids and nickel(0) complexes. Second, we will complete our studies of the mechanisms of carbon-heteroatom bond cleavages by nickel(0) complexes. Thereafter, we shall prepare the final project report.

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6/12/92