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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

DOE/PC/88930--T11

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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 eleventh 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 significant conclusions have been reached during the last quarter: 1) the synergistic effect on the hydrogen transfer between 9,10-dihydroanthracene and diphenylacetylene, as caused by stoichiometric amounts of triisobutylaluminum and bis(1,5-cyclooctadiene)nickel, appears to involve intermediates containing Al-Ni bonds; 2) the catalytic oligomerization of benzonitrile by nickel(0) complexes to diphenylethane and triphenyltriazine derivatives involves $\eta^2$- and $\eta^4$-complexes of nickel(0) with benzonitrile and with diphenyldiazacyclobutadienes, respectively; and 3) the interaction of thiobenzophenone and dichlorodiphenylmethane with nickel(0) requires the generation of nickel-carbene intermediates, as a trapping experiment with benzaldehyde indicates.

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## *QUARTERLY TECHNICAL PROGRESS REPORT*

July 1, 1991

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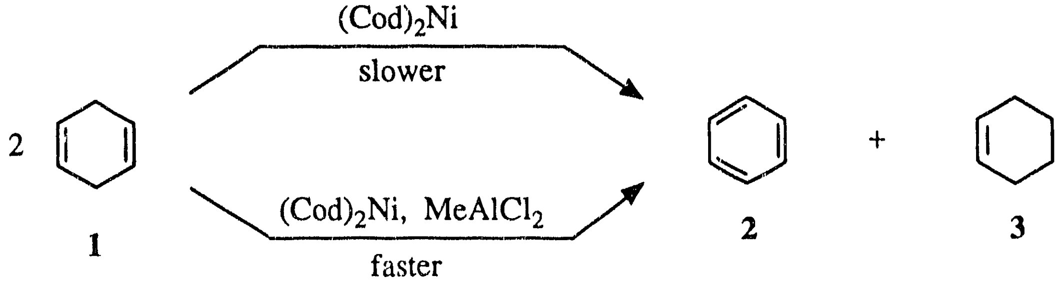
| PERIOD OF PERFORMANCE: | 03/01/91 - 05/31/91 |

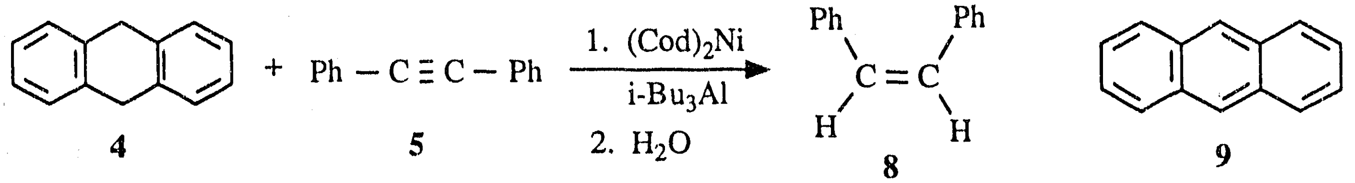
OBJECTIVES: The ultimate objective of this research is to uncover new catalytic processes for the liquefaction of coal and for upgrading coal-derived fuels by removing undesirable organosulfur, organonitrogen and organooxygen constituents. Basic to both the liquefaction of coal and the purification of 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.

PRESENT WORK AND ACCOMPLISHMENTS: Synergistic Hydrogen Transfer. First of all, during the eleventh 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 homomolecular hydrogen transfer, we have now confirmed an instance of heteromolecular 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.

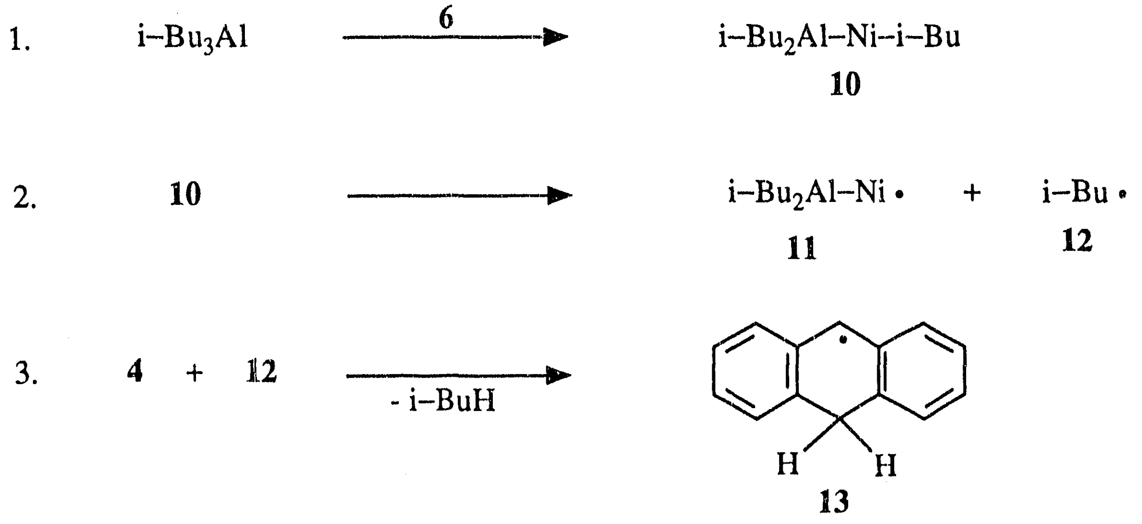


(2)

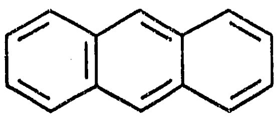
Unexpectedly, when the ratio of triisobutylaluminum used in such a hydrogen transfer reaction was reduced to 0.33 and the ratio of **4**, **5** and **6** was maintained at 1 : 1 : 1, the diphenylacetylene was still completely converted to cis-stilbene (**8**) but the 9,10-dihydroanthracene (**4**) was 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.

For the first case, 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**



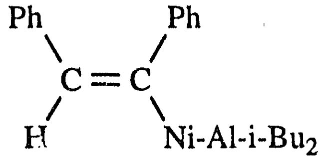
4. **13** + **11** $\longrightarrow$



**9**

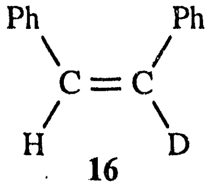
\+ i–$Bu_2$Al--Ni–H **14**

5. **14** + Ph–C≡C–Ph $\longrightarrow$



**15**

6. **15** $\xrightarrow{D_2O}$



**16**

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).

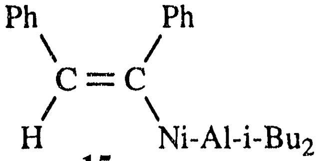
For the second case, catalysis by a 0.33 : 1.0 stoichiometric amount **7** and **6** <u>without</u> the involvement of 9,10-dihydroanthracene and with the formation of isobutene, an alternative mode of decomposition for intermediate **10** (step 2) is suggested in Scheme II:

**Scheme II**

2′. i–$Bu_2$Al-Ni-i-Bu $\rightleftharpoons$ i–$Bu_2$Al-Ni-H + $H_2C{=}CMe_2$

**14** **16**

3′. Ph–C≡C–Ph $\xrightarrow{14}$

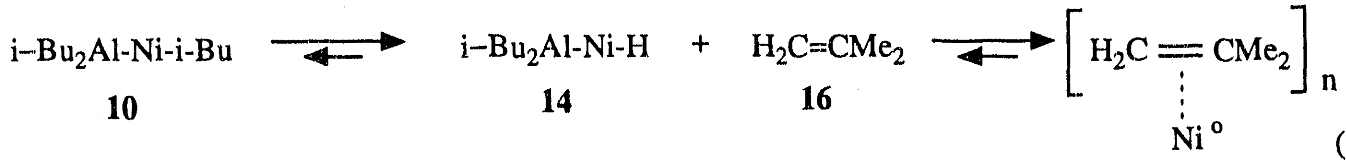


**15**

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-$Bu_3$Al (1.0 : 0.33), Ni(0) scavenges free radicals (step 2) and thus prevents their attack on **4** (step 3) (eq. 3):

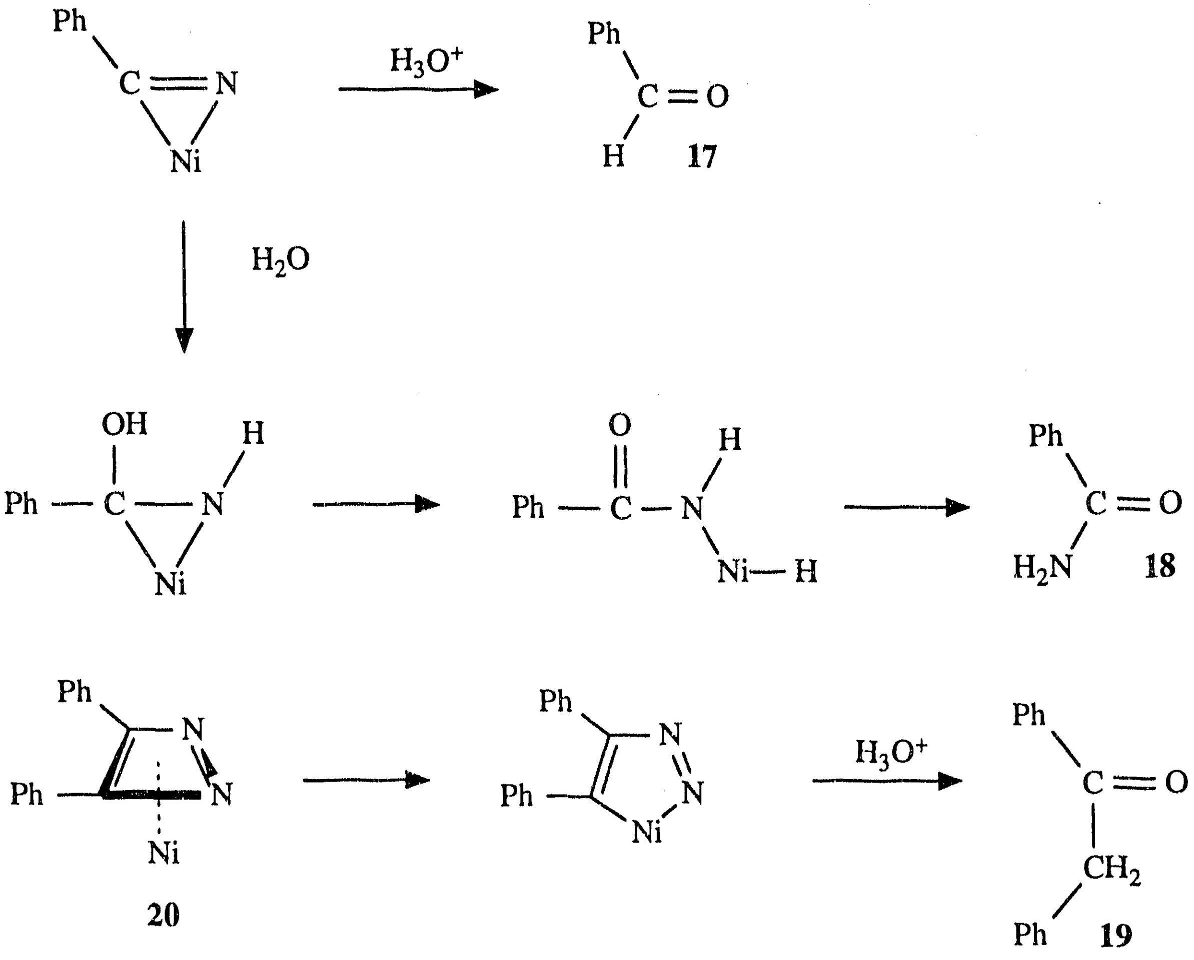
$$\underset{\mathbf{12}}{2\,\text{i–Bu}\,\bullet} + \underset{\mathbf{6}}{\text{Ni}^{o}} \longrightarrow \text{i–Bu}_2\text{Ni} \qquad (3)$$

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



$$\underset{\mathbf{10}}{\text{i-Bu}_2\text{Al-Ni-i-Bu}} \rightleftarrows \underset{\mathbf{14}}{\text{i-Bu}_2\text{Al-Ni-H}} + \underset{\mathbf{16}}{H_2C{=}CMe_2} \rightleftarrows \left[\overset{\displaystyle H_2C = CMe_2}{\underset{\displaystyle Ni^{o}}{\vdots}}\right]_n \qquad (4)$$

Oligomerization of Benzonitrile. The prolonged action of nickel(0) complex **6** in THF leads to an interesting array of products after the reaction mixture is hydrolyzed. Thus far, benzaldehyde (**17**), benzamide (**18**), benzyl phenyl ketone (**19**) and 2,4,6-triphenyltriazine (**22**) have been identified as products. The first three compounds are thought to arise by hydrolysis of nickel(0) complexes. (eqs. 5 - 7):

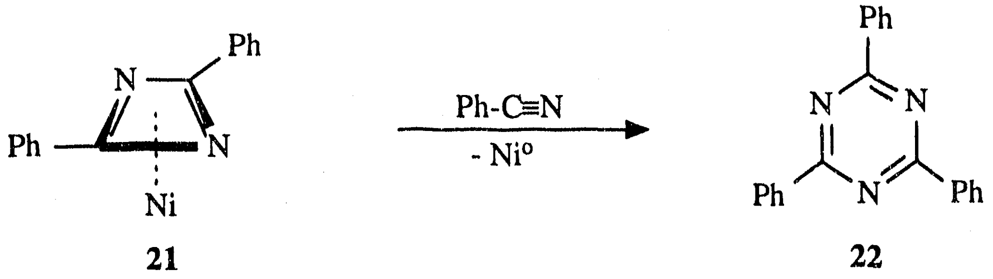


**17** (5)

**18** (6)

**20** **19** (7)

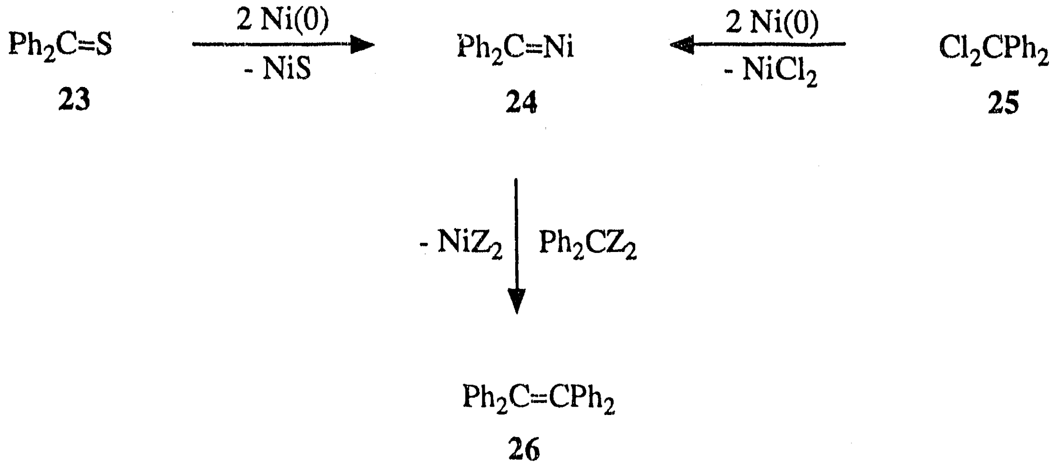
As an alternative to 1,2-diazacyclobutadiene intermediate **20** (formed by a nickel(0)-induced coupling of benzonitrile), two benzonitriles could be coupled to produce 1,3-diazacyclobutadiene complex **21**. Reaction of **21** with a further benzonitrile could yield triazine **22** and regenerate nickel(0) to carry on the catalytic trimerization (eq. 8):



(8)

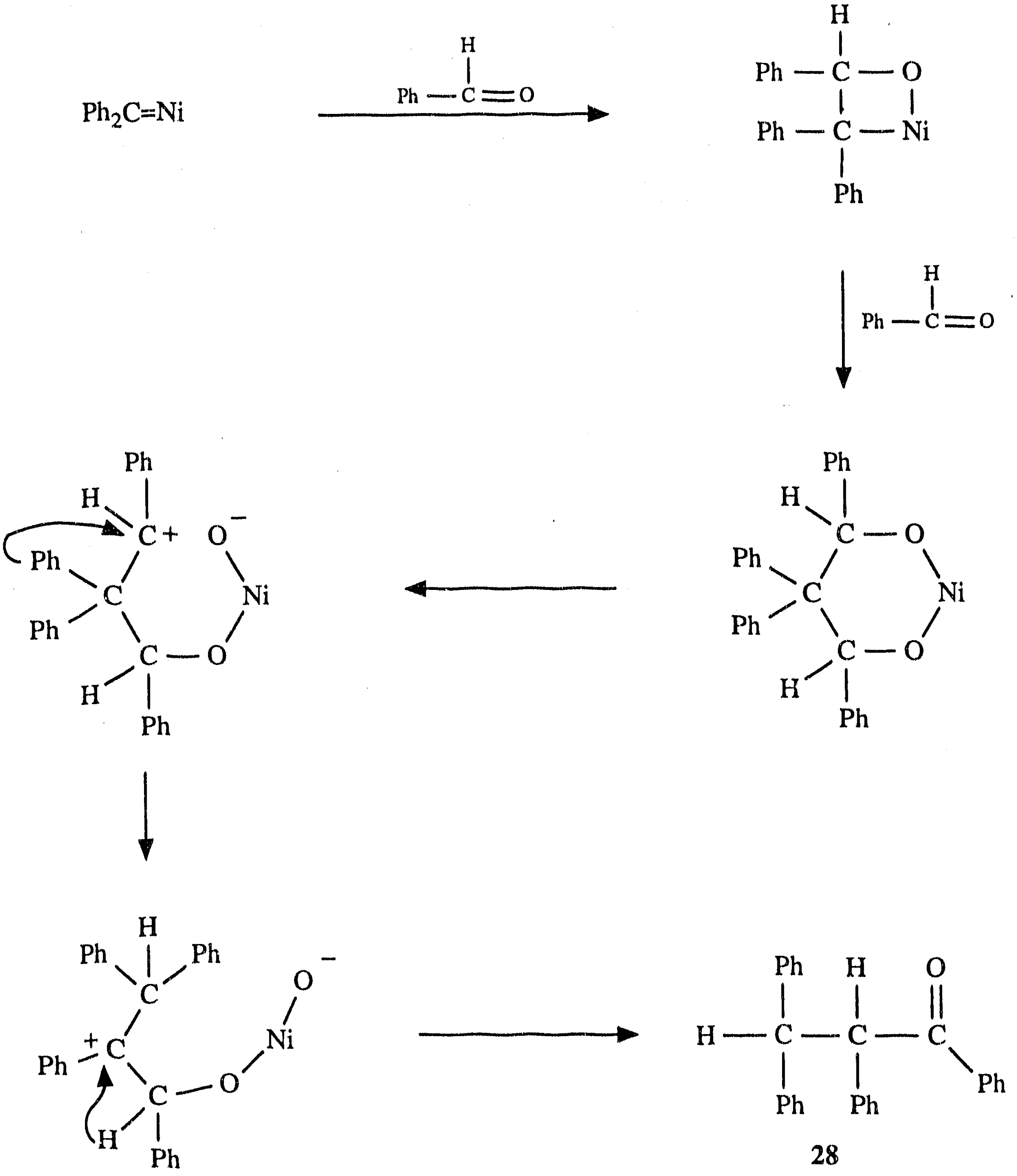
Nickel-Carbene Intermediates. In either the desulfurization of thiobenzophenone (23) or the dechlorination of dichlorodiphenylmethane (25), both of which processes produce **26**, it has been speculated that nickel-carbene **25** (Scheme III) is the crucial intermediate:

**Scheme III**



In order to test this hypothesis, attempts were made to intercept intermediate **24** by insertion of benzaldehyde (**27**) into the putative C=Ni bond of **24**. Work-up of such a trapping experiment yielded **28**, a product consistent with such an insertion (Scheme IV):

### Scheme IV



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PLANS FOR THE NEXT QUARTER: First, we shall further study synergistic catalysis of hydrogen transfer and of desulfurization as promoted by combinations of Lewis acids and nickel(0) complexes. Second, we will continue our studies of the mechanisms of carbon-heteroatom bond cleavages by nickel(0) complexes.

# END

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