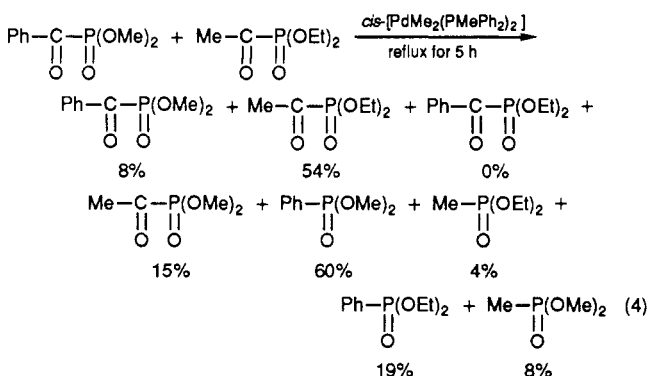


(O)(OMe)<sub>2</sub>, respectively, both of which may be generated by metathesis between (Ph)C(O)P(O)(OMe)<sub>2</sub> and (tol)C(O)P(O)(OEt)<sub>2</sub>.

Additional results were obtained from the reaction of (Ph)C(O)P(O)(OMe)<sub>2</sub> and (Me)C(O)P(O)(OEt)<sub>2</sub> with a catalytic amount of 1 (refluxing in toluene for 5 h) (eq 4).



In addition to the starting  $\alpha$ -ketophosphonates and their direct decarbonylation products, three kinds of phosphorus compounds, (Ph)P(O)(OEt)<sub>2</sub>, (Me)C(O)P(O)(OMe)<sub>2</sub>, and (Me)P(O)(OMe)<sub>2</sub>, were detected. Although the other expected product of the metathesis, (Ph)C(O)P(O)(OEt)<sub>2</sub>, was not detected, the decarbonylation product, (Ph)P(O)(OEt)<sub>2</sub> was observed.

In a similar fashion the reaction of (Et)C(O)P(O)(OMe)<sub>2</sub> and (Me)C(O)P(O)(OEt)<sub>2</sub> in the presence of 1 (refluxing in toluene for 24 h) leads to the formation of two additional  $\alpha$ -ketophosphonates and four phosphonates in low yield.<sup>16</sup>

Investigations into the mechanism of transition-metal-promoted decarbonylation and metathesis of  $\alpha$ -ketophosphonates are currently under way.

**Acknowledgment.** We thank Akira Mizuno and Yoshihisa Toda in Materials Science & Analysis Laboratories, Mitsui Petrochemical Industries, LTD., for <sup>31</sup>P NMR measurements. H.N. acknowledges financial support from the Ministry of Education under Grant No. 63740340.

**Supplementary Material Available:** A table of <sup>1</sup>H and <sup>31</sup>P NMR data for phosphonates (1 page). Ordering information is given on any current masthead page.

(16) The yields of the methathesis products and the decarbonylation products were 1-8%.

## Catalytic and Stoichiometric Formation of Cyclooctatetraenes from Soluble Nickel Complexes

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**Summary:** A benzene-soluble, catalytically active material of composition {(PhC)<sub>2</sub>Ni}<sub>12-13</sub> is isolated by gel-permeation chromatography from the Reppe cyclo-tetramerization of phenylacetylene with Ni(acac)<sub>2</sub>/CaC<sub>2</sub> or NiBr<sub>2</sub>/CaC<sub>2</sub>. Possible steps in the catalytic process are modeled in stoichiometric reactions.

The Reppe reaction, producing cyclooctatetraene (COT) from acetylene with a variety of nickel catalysts, is now more than 40 years old.<sup>1</sup> Despite that, it is a reaction for which mechanistic details are still being investigated.<sup>2-4</sup>

The purpose of this communication is to report the isolation and independent preparation of a hydrocarbon-soluble, oligomeric catalyst from the Reppe reaction of phenylacetylene and to describe some stoichiometric modeling of its reactions.

A study on the catalytic cyclooligomerization of phenylacetylene to 1,2,4-triphenylbenzene and 1,3,5,8-cyclooctatetraene (1)<sup>5</sup> by Ni(acac)<sub>2</sub>/CaC<sub>2</sub> or Ni(Br)<sub>2</sub>/CaC<sub>2</sub> revealed formation of a benzene-soluble material that had an elemental composition corresponding to {(PhC)<sub>2</sub>Ni}<sub>n</sub>. This material, which could be isolated by gel-permeation chromatography, had a molecular weight of 3250 ± 290, corresponding to a value near 13 for *n* in the above formula. Various preparations of the material had magnetic properties ranging from diamagnetism to weak paramagnetism, with the maximum magnetic moment, as determined by the Evans' method,<sup>6</sup> being 3.77  $\mu_B$ .

The material was shown to be an active catalyst, leading to triphenylbenzene and Ph<sub>4</sub>-COT formation from phenylacetylene, without any apparent induction period.<sup>7</sup> Its isolation from the chromatography presumably precludes catalysis by adventitious colloidal nickel. An apparently identical material (as judged by IR and elemental composition) could be prepared in 60% yield by reaction of 2 equiv of PhCCLi with (1,2-dimethoxyethane)NiCl<sub>2</sub> in THF at -70 °C.<sup>8</sup>

Hydrolysis of the catalyst with concentrated aqueous HCl afforded a tarry oligomeric hydrocarbon but did not yield any phenylacetylene, suggesting that the catalyst was not an oligomer of nickel(II) bis(phenylacetylidyne). This conclusion was reinforced by the observation that treatment with bis(diphenylphosphino)ethane (diphos) resulted in the formation of (diphos)<sub>2</sub>Ni<sup>0</sup> (corresponding to about 30% of the theoretical amount of Ni). Preparation of the catalyst with C<sub>6</sub>D<sub>5</sub>CCLi and reaction with 5 equiv of C<sub>6</sub>H<sub>5</sub>CCH resulted in formation of triphenylbenzene and Ph<sub>4</sub>-COT containing ≤1% deuterium again suggesting that the original phenylacetylidyne unit was no longer present in that form in the catalyst.

When the catalyst was used to oligomerize (*o*-allylphenyl)acetylene, the resulting tetramer (formed catalytically as a mixture of stereoisomers and accompanied by several minor products of as yet unknown structure) was

(1) Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Justus Liebig's Ann. Chem.* 1948, 560, 1.

(2) Schrauzer, G. N. *Chem. Ber.* 1961, 94, 1403.

(3) Vollhardt, K. P. C.; Colborn, R. E. *J. Am. Chem. Soc.* 1986, 108, 5470.

(4) Wilke, G. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 185 and references therein.

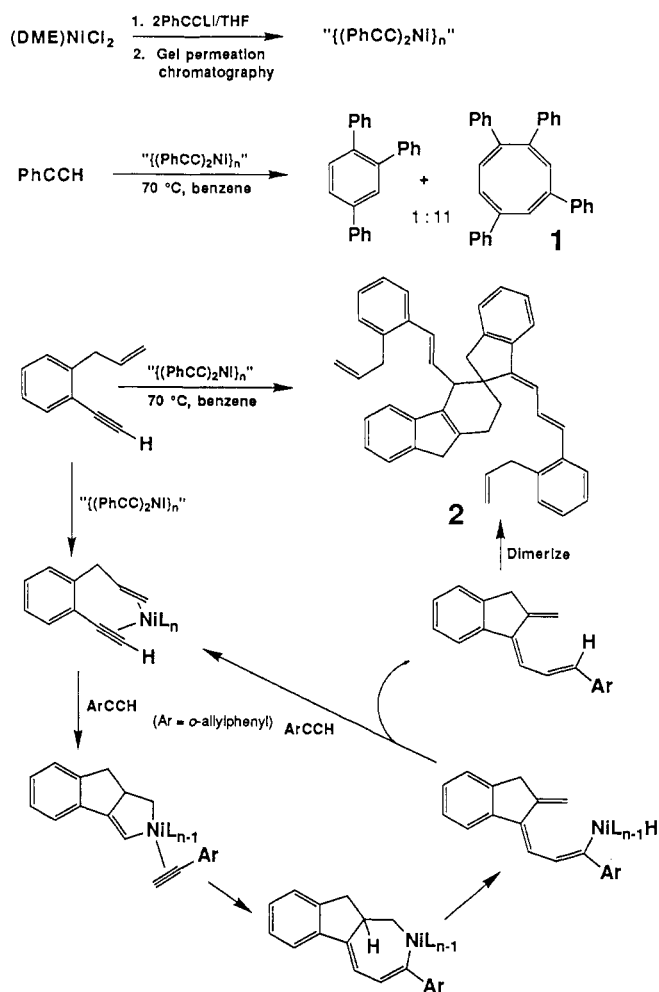
(5) A substituted COT has to be numbered in a way that specifies the particular bond-shift isomer. In the present case, evidence from the stoichiometric reactions suggests that it is undesirable to have a double bond between neighboring phenyl groups in a Ph<sub>4</sub>-COT, which is why the particular isomer shown in Scheme 1 has been selected. The possibility that it is really 1,2,4,6-tetraphenylcyclooctatetraene cannot be rigorously excluded, however.

(6) Evans, D. *J. Chem. Soc.* 1959, 2003.

(7) In a typical result, 5 mg of the catalyst converted a solution of 120 mg of phenylacetylene in 1 mL of benzene to 8.9 mg of triphenylbenzene and 98.9 mg of Ph<sub>4</sub>-COT after 15 h at 70 °C.

(8) It is possible that this material is the same as that prepared by Nast et al. (Nast, R.; Vester, K.; Griesshammer, H. *Chem. Ber.* 1957, 90, 2678), although the magnetic susceptibility determined by these workers would suggest a higher magnetic moment than that determined in the present work. No study of catalytic activity with acetylenes was reported by the Nast group. It may also be that the Reppe catalyst prepared from reaction of nickel atoms with phenyl acetylene is related to the present material (Simons, L. H.; Lagowski, J. J. *Fundam. Res. Homogeneous Catal.* 1978, 2, 73).

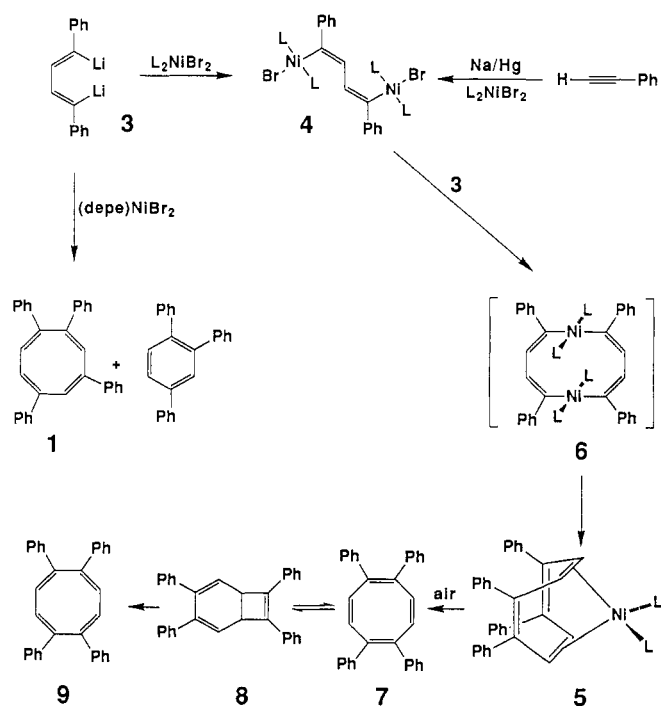
## Scheme I. Preparation and Reactions of the Catalyst



found to have the structure 2. This can be seen to be a Diels–Alder dimer, each half of which is itself a dimer of the original acetylene and for which a plausible mechanism of production can be suggested, provided that the nickel is in the zero oxidation state (Scheme I).

If the formation of trimer and tetramer occurred from a common mononuclear complex, one would expect that the benzene:COT ratio would decrease in proportion to the acetylene concentration because the metallacycloheptatriene that would appear to be a necessary intermediate could reductively eliminate to benzene in a unimolecular step or ring expand to the metallacyclononatetraene in a step that was overall bimolecular. A dinuclear mechanism (such as that suggested by Wilke<sup>4</sup>) might lead to the opposite dependence of the benzene:COT ratio on acetylene concentration because the crucial intermediate (in Wilke's mechanism, with two neighboring nickelacyclopentadienes<sup>4</sup>) could reductively eliminate to COT or be intercepted to give benzene by attack of an external acetylene. A clear direct proportionality is not required in this case because the benzene could also be formed from mononuclear precursors. In practice it was found that the homogenous catalyst afforded triphenylbenzene and Ph<sub>4</sub>-COT in a ratio whose dependence on phenylacetylene concentration had a slope of only  $(2.1 \pm 0.6) \times 10^{-3} \text{ M}^{-1}$ . This is not consistent with a mononuclear mechanism but could be consistent with either the Wilke mechanism or some other dinuclear process.

In efforts to model some steps in this catalytic process, we investigated the reaction of  $(\text{Et}_3\text{P})_2\text{NiBr}_2$  with (*E,E*)-1,4-dithio-1,4-diphenyl-1,3-butadiene (3) at  $-78^\circ\text{C}$  in

Scheme II<sup>a</sup>

<sup>a</sup>The ligand L is triethylphosphine; depe is 1,2-bis(diethylphosphino)ethane.

THF.<sup>9,10</sup> The products were found to be complexes 4 and 5.<sup>11</sup> The yield of 4 was 13% if a 1:1 ratio of reactants was used, but 80% if the ratio was 2:1. Complex 5 could be produced in 92% yield from 4 by reaction with 3, a reaction that presumably occurs via dimetallacycle 6, although no such intermediate could be isolated (see Scheme II). Decomposition of 5 in air led to quantitative formation of 1,2,5,6-tetraphenylcyclooctatetraene (7) which rapidly rearranged (presumably reversibly) to 3,4,7,8-tetraphenylbicyclo[4.2.0]octa-2,4,7-triene (8) and slowly rearranged to 1,4,5,8-tetraphenylcyclooctatetraene (9).

The potential significance of this chemistry with regard to the mechanism of the Reppe reaction was made apparent when it was discovered that 4 could be prepared (albeit in only 12% yield) by treatment of phenylacetylene with  $(\text{Et}_3\text{P})_2\text{NiBr}_2$  and 2% Na/Hg at  $20^\circ\text{C}$  in THF. The possibility that this could have occurred by reduction of phenylacetylene to a disodium analogue of 3 with Na/Hg was ruled out when it was determined that a mixture of these two afforded no detectable 1,4-diphenyl-1,3-butadiene upon aqueous workup. Apparently the acetylene coupling occurs only in the presence of the nickel. Perhaps most intriguing of all was the finding that treatment of  $(\text{depe})\text{NiBr}_2$  (depe = 1,2-bis(diethylphosphino)ethane) with 3 at  $-78^\circ\text{C}$  in THF yielded, *inter alia*, 1,2,4-triphenylbenzene and 1,3,5,8-tetraphenylcyclooctatetraene (1). First, these are precisely the products formed in the catalytic cyclooligomerization of phenylacetylene. Second,

(9) (a) Reich, H. J.; Reich, I. L. *J. Org. Chem.* **1976**, *40*, 2248. (b) Atwell, W. H.; Weyenburg, D. R.; Gilman, H. J. *J. Org. Chem.* **1967**, *32*, 885. (c) Weyenburg, D. R.; Toporcer, L. H.; Bey, A. E. *J. Org. Chem.* **1965**, *30*, 4096.

(10) Calculations have suggested that the parent (*Z,Z*)-1,4-dithio-butadiene has a bridged, cyclic structure (Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1980**, *102*, 7928) and recent experimental evidence suggests that the (*Z,Z*) configuration is the most stable, perhaps because of the favorability of this structure (Ashe, A. J., III; Mahmoud, S. *Organometallics* **1988**, *7*, 1878). Apparently the tetraphenyl derivative does have such a structure (footnote 2 in Ashe/Mahmoud reference) and so it is quite possible that 3 does, too.

(11) Both complexes were identified by X-ray crystallography.

the reaction clearly requires cleavage of the C2-C3 bond of the diphenylbutadienyl unit in a process with little precedent. The depe analogue of 4, which could be prepared by reaction of 4 with depe, could be shown *not* to be an intermediate in this reaction, since it did not afford 1 or triphenylbenzene upon treatment with compound 3.

There is a possibility that these stoichiometric reactions are mechanistically related to those occurring in the catalytic process. The synthesis of 4 from phenylacetylene and the apparently facile reductive elimination of 6 to a cyclooctatetraene suggest a plausible alternative to the Wilke mechanism for the Reppe reaction, in which C-C bond formation occurs between acetylenes on different nickel atoms, to give a dimetallacycle like 6.<sup>12</sup> On the other hand, it is tempting to suggest that the reaction of 3 with (depe)NiBr<sub>2</sub> occurs via nickelacyclopentadienes,<sup>13</sup> if so, the identity of the products with those observed catalytically would tend to support the Wilke proposal. Until the details of these homogeneous reactions have been elucidated, however, the choice between Wilke's mechanism and alternative dinuclear processes cannot be made conclusively. Experiments designed to assist in this differentiation are currently in progress.

**Acknowledgment.** We thank Ms. Heidi Dankosh for technical assistance, Dr. László Párkányi for assistance with the X-ray crystallography, and the National Science Foundation for a predoctoral fellowship to K.P.G.

**Supplementary Material Available:** Tables of bond distances, bond angles, crystal data, fractional coordinates and isotropic thermal parameters, and anisotropic thermal parameters for 4 and 5 and a table of torsional angles for 5 (26 pages). Ordering information is given on any current masthead page.

(12) For an alternative dinuclear coupling of acetylenes, see: Diercks, R.; Stamp, L.; Kopf, J.; tom Dieck, H. *Angew. Chem., Int. Ed. Engl.* 1984, 23, 893.

(13) (a) Eisch, J. J.; Piotrowski, A. M.; Han, K. I.; Krüger, C.; Tsay, Y. H. *Organometallics* 1985, 4, 224. (b) Eisch, J. J.; Galle, J. E.; Aradi, A. A.; Boleslawski, M. P. *J. Organomet. Chem.* 1986, 312, 399.

## Insertion of an Ynamine into the C-N Bond of a (Dimethylamino)carbene Ligand

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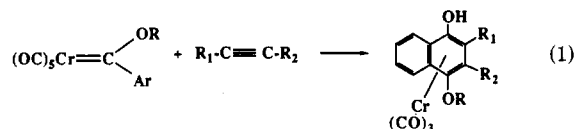
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**Summary:** Insertion of the ynamine MeC<sub>2</sub>NMe<sub>2</sub> into the C-N bond of the (dimethylamino)carbene ligand in the cluster complex Os<sub>3</sub>(CO)<sub>8</sub>[C(H)NMe<sub>2</sub>]<sub>2</sub>(μ<sub>3</sub>-S)(μ-H)<sub>2</sub> (1) has yielded the product Os<sub>3</sub>(CO)<sub>8</sub>[C(H)=C(Me)C(NMe<sub>2</sub>)<sub>2</sub>] (2, 75%) that contains a terminally coordinated amidinium-substituted propenyl ligand. Complex 2 was characterized by IR, <sup>1</sup>H NMR, and single-crystal X-ray diffraction analysis.

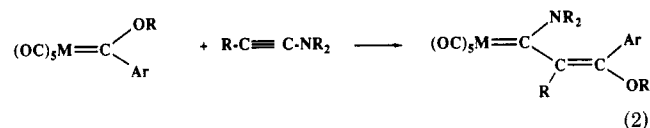
Over the years, heteroatom-substituted carbene ligands have been a source of great interest because of their unusual structures and bonding and more recently because of their novel applications in organic synthesis.<sup>1-3</sup> Metal

(1) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Chemistry*; Verlag Chemie: Weinheim, West Germany, 1983.

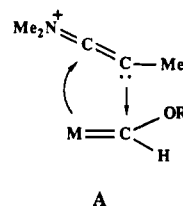
complexes containing alkoxyarylcarbene ligands react with alkynes and CO in an unusual annulation reaction to yield benz-fused hydroquinone ether complexes (eq 1).<sup>2-4</sup>



Variations of this reaction have been successfully used in the synthesis of the vitamins E and K<sup>3a</sup> and the antibiotics nanaomycin and deoxyfrenolicin.<sup>6</sup> In these reactions, it is generally agreed that the alkyne addition to the carbene proceeds by an initial coordination of the alkyne to the metal atom. In contrast, nucleophilic alkynes such as ynamines, RC≡CNR<sub>2</sub>, have been shown to react with alkoxy-carbene complexes by insertion into the metal-carbene, M-C, bond (eq 2).<sup>7</sup> This reaction has been shown



to occur by a direct addition of the alkyne to the electron-deficient carbene center; see intermediate A.<sup>7a</sup>



Due to their lower reactivity, the reactions of (dialkylamino)carbene ligands with alkynes have been studied relatively little.<sup>4,7b,8</sup> We now wish to report the preliminary results of our investigation of the reaction of the amino-carbene-containing cluster complex Os<sub>3</sub>(CO)<sub>8</sub>[C(H)NMe<sub>2</sub>]<sub>2</sub>(μ<sub>3</sub>-S)(μ-H) (1) with MeC≡CNMe<sub>2</sub> which we have found to yield the complex Os<sub>3</sub>(CO)<sub>8</sub>[C(H)C(Me)C(NMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>(μ<sub>3</sub>-S)(μ-H)<sub>2</sub> (2) formed by the insertion of the ynamine molecule into the C-N bond of the carbene ligand.

1 (25 mg) was allowed to react with 40 μL of MeC≡CNMe<sub>2</sub> in refluxing heptane solvent for 2 h. The product 2 was isolated in 75% yield by TLC on silica gel using a CH<sub>2</sub>Cl<sub>2</sub>/hexane (7/3) solvent mixture. Compound 2 was characterized by IR, <sup>1</sup>H NMR, and single-crystal X-ray diffraction analyses.<sup>10,11</sup> An ORTEP diagram of the mo-

(2) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books, Mill Valley, CA, 1987; Chapter 16.

(3) (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* 1984, 23, 587. (b) Dötz, K. H. *Pure Appl. Chem.* 1983, 55, 1689.

(4) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. J. *Organomet. Chem.* 1987, 334, 9.

(5) Semmelhack, M. F.; Bozell, J. J. *Tetrahedron Lett.* 1982, 23, 2931.

(6) Semmelhack, M. F.; Bozell, J. J.; Sato, T.; Wulff, W.; Spiess, E.; Zask, A. *J. Am. Chem. Soc.* 1982, 104, 5850.

(7) (a) Fischer, H.; Dötz, K. H. *Chem. Ber.* 1980, 113, 193. (b) Dötz, K. H.; Fügen-Köster, B.; Neugebauer, D. *J. Organomet. Chem.* 1979, 182, 489. (c) Dötz, K. H.; Kreiter, C. G. *Chem. Ber.* 1976, 109, 2026.

(8) Yamashita, A. *Tetrahedron Lett.* 1986, 27, 5915.

(9) Adams, R. D.; Kim, H. S.; Wang, S. *J. Am. Chem. Soc.* 1985, 107, 6107.

(10) IR (hexane, cm<sup>-1</sup>): 2076 (m), 2038 (vs), 2014 (s), 1993 (s), 1976 (s), 1950 (m). <sup>1</sup>H NMR (δ in CDCl<sub>3</sub>): 9.19 (m, 1 H), 3.07 (s, 12 H), 2.07 (d, 3 H, J<sub>H-H</sub> = 0.6 Hz), -20.04 (d, 1 H, J<sub>H-H</sub> = 2.2 Hz), -20.51 (s, 1 H). Elemental anal. Calcd: C, 19.12; H, 1.93; N, 2.97. Found: C, 19.91; H, 1.93; N, 2.80.