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.[12] On the other hand, it is tempting to suggest that the reaction of 3 with (depe)NiBr$_2$ occurs via nickelacyclopentadienes,[13] 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. Lâszlô Pârkânyi 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.

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

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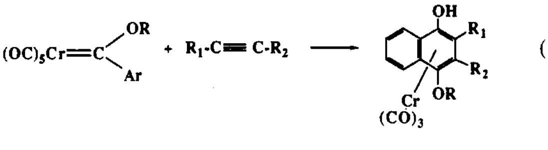
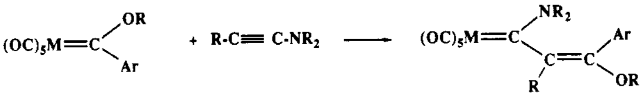
Summary: Insertion of the ynamine MeC_2NMe_2 into the C–N bond of the (dimethylamino)carbene ligand in the cluster complex $Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (**1**) has yielded the product $Os_3(CO)_8[C(H){=}C(Me)C(NMe_2)_2]$ (**2**, 75%) that contains a terminally coordinated amidinium-substituted propenyl ligand. Complex **2** was characterized by IR, ^1H 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.[1-3] Metal complexes containing alkoxyarylcarbene ligands react with alkynes and CO in an unusual annulation reaction to yield benz-fused hydroquinone ether complexes (eq 1).[2-4]

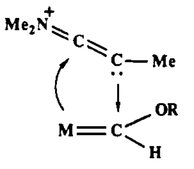


(1)

Variations of this reaction have been successfully used in the synthesis of the vitamins E and K[3a] and the antibiotics nanaomycin and deoxyfrenolicin.[6] 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, $RC\equiv CNR_2$, have been shown to react with alkoxycarbene complexes by insertion into the metal–carbene, M–C, bond (eq 2).[7] This reaction has been shown to occur by a direct addition of the alkyne to the electron-deficient carbene center; see intermediate A.[7a]



(2)



A

Due to their lower reactivity, the reactions of (dialkylamino)carbene ligands with alkynes have been studied relatively little.[4,7b,8] We now wish to report the preliminary results of our investigation of the reaction of the aminocarbene-containing cluster complex $Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)$ (1) with $MeC\equiv CNMe_2$ which we have found to yield the complex $Os_3(CO)_8[C(H)C(Me)C(NMe_2)_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (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 $MeC\equiv CNMe_2$ in refluxing heptane solvent for 2 h. The product 2 was isolated in 75% yield by TLC on silica gel using a CH_2Cl_2/hexane (7/3) solvent mixture. Compound 2 was characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses.[10,11] An ORTEP diagram of the mo-

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(10) IR (hexane, cm^{-1}): 2076 (m), 2038 (vs), 2014 (s), 1993 (s), 1976 (s), 1950 (m). ^1H NMR (δ in $CDCl_3$): 9.19 (m, 1 H), 3.07 (s, 12 H), 2.07 (d, 3 H, J_{H-H} = 0.6 Hz), −20.04 (d, 1 H, J_{H-H} = 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.

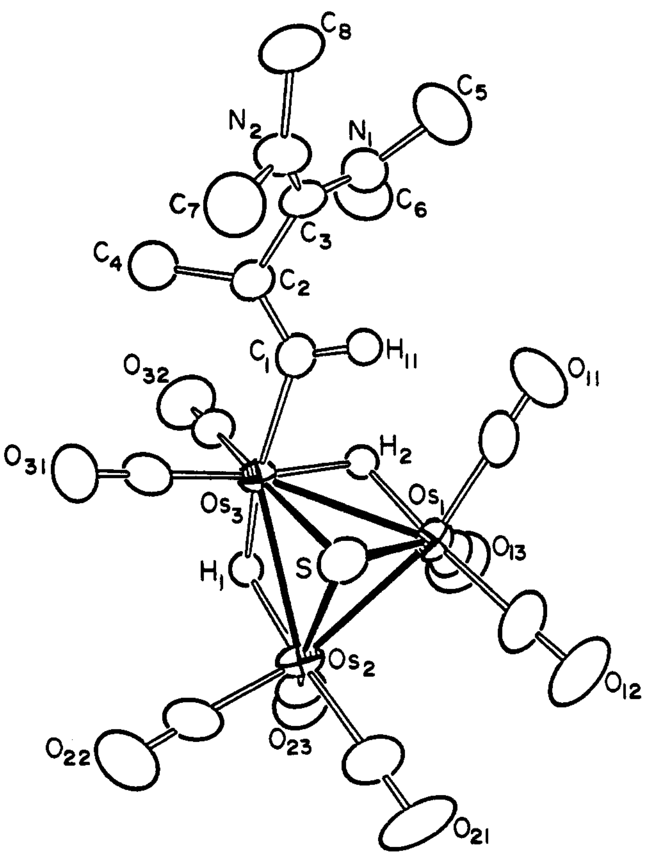
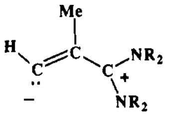


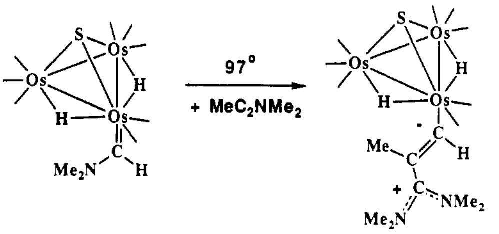
Figure 1. An ORTEP diagram of $Os_3(CO)_8[C(H){=}C(Me)C(NMe_2)_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ (2) showing 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: Os(3)–C(1) = 2.067 (9), C(1)–C(2) = 1.34 (1), C(2)–C(3) = 1.48 (1), C(3)–N(1) = 1.32 (1), C(3)–N(2) = 1.32 (1), Os(3)–C(1)–C(2) = 133.6 (6), C(1)–C(2)–C(3) = 119.2 (7), N(1)–C(3)–N(2) = 121.9 (8).

lecular structure of 2 is shown in Figure 1. The $Os_3(CO)_8(\mu_3\text{-}S)(\mu\text{-}H)_2$ cluster contains two bridging hydride ligands which structurally is virtually identical with that grouping in compound 1.[9] The most interesting ligand is the $HC{\equiv}C(Me)C(NMe_2)_2$ grouping that is terminally coordinated to the metal atom Os(3). This group could be viewed as an amidinium-substituted propenyl ligand B



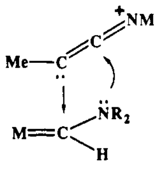
B

that serves as a two-electron donor to Os(3). The C(1)–C(2) distance is short, 1.34 (1) Å, and characteristic of a C–C double bond. The C(2)–C(3) bond of 1.48 (1) Å is only slightly shorter than that of a C–C single bond. The two C–N bond distances to C(3) are identical, 1.32 (1) Å, and both nitrogen atoms exhibit a planar geometry. Both features are consistent with the existence of partial multiple bonding of the amino groups to the carbon C(3) to stabilize the formal positive charge. The plane of the amidinium group is rotated 62° from the plane of the propenyl ligand which indicates a lack of conjugation between these two groupings. The only previous report of an insertion of an alkyne into a heteroatom–carbon bond of a carbene ligand was for the insertion of an ynamine into a C–O bond of the chelating bis(ethoxycarbene)tungsten carbonyl complex $(CO)_4\overline{W[C(OEt)C(H)PhC(H)PhC}(OEt)]$.[12]



1 2 (3)

The formation of 2 (eq 3) is believed to occur by a direct addition of the β-carbon atom of ynamine to the carbene carbon, C, but unlike the M–C insertion, it is the dialkylamino group of the carbene ligand that is shifted to the α-carbon atom. Studies to investigate the effect of variation of the substituents on the carbene and the ynamine on the course of this reaction are in progress.



C

Acknowledgment. This research was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy.

Supplementary Material Available: Tables of crystal data, positional parameters, intramolecular bond distances and angles, and anisotropic thermal parameters of compound 2 (9 pages); a listing of structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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(11) Pale yellow crystals of 2 were grown from solutions in CH_2Cl_2 solvent by cooling to −20 °C. These crystals belonged to the triclinic crystal system: space group $P\bar{1}$; a = 11.038 (2) Å, b = 12.831 (3) Å, c = 9.991 (2) Å, α = 98.16 (2)°, β = 108.43 (1)°, γ = 112.00 (1)°, Z = 2. Diffraction data were collected on a Rigaku AFC6S diffractometer by using Mo Kα radiation. Calculations were performed on a MICROVAX II computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Data were corrected for absorption. The structure was solved by the heavy-atom method and was refined (2954 reflections) to the final values of the residuals, R = 0.024 and R_w = 0.028. The hydride ligands were located and refined on their positional parameters only. All other hydrogen atom positions were calculated.

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An η^4-Thiophene Ligand. A New Mode of Thiophene Coordination in Cp*Ir(η^4-2,5-dimethylthiophene)

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Summary: A two-electron reduction of the 18-electron complex $Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2T)^{2+}$, where 2,5-$Me_2T$ is 2,5-dimethylthiophene, produces $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$, which contains the novel η^4-thiophene ligand. An X-ray study shows that the η^4-2,5-Me_2T ligand is coordinated to the metal via only the four carbon atoms. The uncoordinated sulfur atom is sufficiently basic to form a strong adduct with BH_3.