of hours to give a number of products depending on factors such as concentration, solvent, and temperature. Study of these additional species is in progress in the hope of observing intermediates in the reduction of coordinated SO_2.

Acknowledgment. This work was carried out under the auspices of the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences.

Registry No. $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-}SO_2)$, 91002-40-3; $H_2Os_3(CO)_{10}$, 41766-80-7.

Supplementary Material Available: A table of anisotropic thermal parameters and a listing of calculated and observed structure factors (19 pages). Ordering information is given on any current masthead page.

Communications

Alkyne Insertion Reactions in Nickel Acyl Complexes. Occurrence of a 1,2-Trimethylphosphine Shift and the X-ray Structures of $Ni[C(Ph){=}C(H)(COCH_2SiMe_3)]Cl(PMe_3)_2$ and $Ni[C(Ph)(PMe_3)C(H)(COCH_2CMe_2Ph)]Cl(PMe_3)$

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Summary: The facile formation of $Ni[C(Ph){=}C(H)(COR)]Cl(PMe_3)_2$ complexes (R = CH_3 (**1a**), CH_2SiMe_3 (**1b**), CH_2CMe_3 (**1c**), and CH_2CMe_2Ph (**1d**)) by insertion of $PhC{\equiv}CH$ into the Ni—COR bond of the corresponding $NiCl(COR)(PMe_3)_2$ derivatives is reported. Complex **1d** reversibly rearranges in solution to yield the nickelacyclopropane complex $Ni[C(Ph)(PMe_3)C(H)(COCH_2CMe_2Ph)]Cl(PMe_3)$, **2**, which contains a novel ketoylidic ligand. The X-ray structures of **1b** and **2** are also reported.

The insertion of unsaturated hydrocarbons into transition metal–carbon bonds is at present the subject of much academic and industrial research.[2] Recent elegant studies by Bergman et al.[3] have shown that the insertion of alkynes into the Ni–C bond of $Ni(acac)CH_3(PPh_3)$ takes place by a concerted cis addition process, with a reversible 1,3 dissociative shift of PPh_3 being suggested for the formation of trans addition products. In this paper we wish to communicate the facile formation of vinyl ketone complexes $Ni[C(Ph){=}C(H)(COR)]Cl(PMe_3)_2$ (R = CH_3 (**1a**), CH_2SiMe_3 (**1b**), CH_2CMe_3 (**1c**), CH_2CMe_2Ph (**1d**)) (in which the Ni center attains five-coordination by virtue of a strong interaction with the oxygen atom) by insertion of $PhC{\equiv}CH$ into the Ni–COR bond of the corresponding *trans*-$Ni(COR)Cl(PMe_3)_2$ complexes.[4,5] In addition, with the reversible conversion of **1d** into $Ni[C(Ph)(PMe_3)C(H)(COCH_2CMePh)]Cl(PMe_3)$, **2**, which contains a novel ketoylidic ligand, we demonstrate that the 1,2 reversible shifts of phosphine ligands (see Scheme I) operate in systems related to those investigated by Bergman.[3] The X-ray crystal structures of **1b** and **2** are also reported.

The above acyls undergo a smooth reaction[6] with $PhC{\equiv}CH$ to afford moderate yields (ca. 40–50%) of the vinyl complexes **1a–d**.

$$trans\text{-}NiCl(COR)(PMe_3)_2 \xrightarrow{PhC\equiv CH} trans\text{-}(Z)\text{-}NiCl[C(Ph){=}CH(COR)](PMe_3)_2$$

1a, R = CH_3
1b, R = CH_2SiMe_3
1c, R = CH_2CMe_3
1d, R = CH_2CMe_2Ph

The reactions are highly regio- and stereoselectives and seem to yield only the trans *Z* derivatives as indicated above. The new compounds are red crystalline solids that are moderately stable to air and soluble in common organic solvents. Spectroscopic data[7] are in accord with the proposed formulations. It is noteworthy to point out that the IR spectra of complexes 1 show ν(C–O) at ca. 1600 cm^{-1} (ca 40–50 cm^{-1} lower than in the parent acyls), suggesting that a change in the coordination mode of the acyl group

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(6) To a stirred solution of $NiCl(COCH_2R)(PMe_3)_2$ (1.5 mmol) in a 2:1 Et_2O–acetone mixture (25 mL), was added an excess of $PhC{\equiv}CH$ (ca. 0.2 mL) via syringe. After the mixture was stirred overnight at room temperature, the volatiles were removed in vacuo and the residue was extracted with Et_2O (30 mL). The resulting solution was centrifuged and the volume partially reduced until incipient crystallization. Cooling at −30 °C afforded the complexes **1a–c** (see ref 11 for **1d**) as red crystals, which were washed with petroleum ether and dried in vacuo; yield ca. 50%.

(7) For example, for **1b**: ^1H NMR (250 MHz, C_6D_6) δ 0.33 (s, 9 H, $CH_2Si\mathit{Me}_3$), 1.00 (pt, $J_{PH(app)}$ = 4 Hz, 18 H, PMe_3), 2.32 (s, 2 H, CH_2SiMe_3), 6.76 (t, $^4J_{PH}$ = 5.2 Hz, 1 H, C(Ph)=C*H*), 7.24 (m, 3 H, *m*-H and *p*-H of C_6H_5 group), 8.40 (d, $^3J_{HH}$ = 8.3 Hz, 2 H, *o*-H of C_6H_5 group); IR (Nujol mull, cm^{-1}) 1600 (ν(CO)), 1490 (ν(C=C)); molecular weight (crioscopically in C_6H_6, N_2), calcd for $C_{19}H_{35}OP_2ClSiNi$ 464, found 425. Anal. Calcd for $C_{19}H_{35}OP_2ClSiNi$: C, 49.2; H, 7.5. Found: C, 48.8; H, 7.5.

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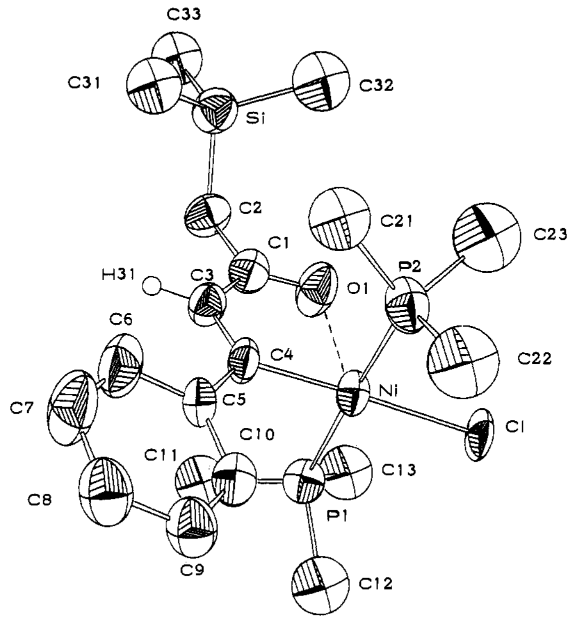


Figure 1. Molecular structure of **1b** and atom labeling scheme. Relevant bond distances (Å) and angles (deg) are as follows: Ni–C(4) = 1.896 (7), Ni–P(1) = 2.191 (3), Ni–Cl = 2.299 (3), Ni–P(2) = 2.189 (3), Ni–O(1) = 2.535 (7), C(1)–O(1) = 1.25 (1), C(1)–C(3) = 1.46 (1), C(3)–C(4) = 1.34 (1); O(1)–Ni–Cl = 105.6 (2), O(1)–Ni–C(4) = 76.9 (3), Ni–C(4)–C(3) = 118.8 (6), C(4)–Ni–P(2) = 89.5 (3), P(2)–Ni–Cl = 90.3 (1), Cl–Ni–P(1) = 89.5 (1), P(1)–Ni–C(4) = 90.5 (2).

has taken place. A strong absorption in the proximity of 1490 cm^{-1}, which is absent in the IR spectra of the parents acyls, can be attributed to the ν(C=C) of the coordinated vinyl groups.

^{1}H NMR studies of equimolar mixtures of *trans*-NiCl(COCH$_2$SiMe$_3$)(PMe$_3$)$_2$ and PhC≡CH show formation of **1b** as the only detectable product. X-ray studies[8] conclusively demonstrate that **1b** is the trans *Z* isomer, possibly resulting from the 1,2 cis addition of the acyl complex to PhC≡CH. The Ni atom is in a five-coordinate distorted square-pyramidal environment (Figure 1) with the keto vinylic oxygen O(1) at a distance of 2.535 (7) Å. Similar contacts have been observed in related complexes.[9] The Ni–O interaction lengthens the corresponding C(1)–O(1) bond to 1.25 (1) Å (1.20 (1) Å in NiCl(COCH$_2$SiMe$_3$)(PMe$_3$)$_2$.[4] Conjugation with the C(3)–C(4) double bond also accounts for the weakening of the carbonyl linkage C(1)–O(1), and the conjugated system O(1)–C(1)–C(3)–C(4) eclipses the Ni–C(4) bond vector.

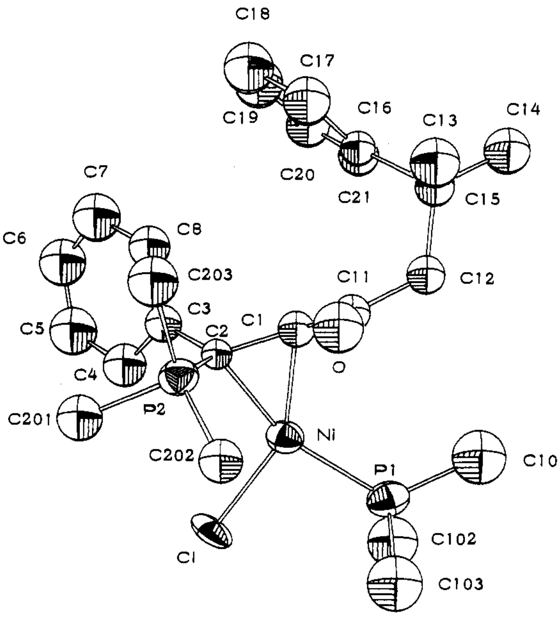


Figure 2. Molecular structure of **2** and atom labeling scheme. Important bond distances (Å) and angles (deg) include the following: Ni–Cl = 2.266 (4), Ni–P(1) = 2.188 (5), Ni–C(1) = 1.97 (1), Ni–C(2) = 1.95 (1), C(1)–C(2) = 1.44 (2), C(2)–P(2) = 1.77 (1); C(1)–Ni–C(2) = 43.2 (6), C(1)–Ni–P(1) = 117.4 (5), P(1)–Ni–Cl = 93.8 (2), Cl–Ni–C(2) = 105.7 (4).

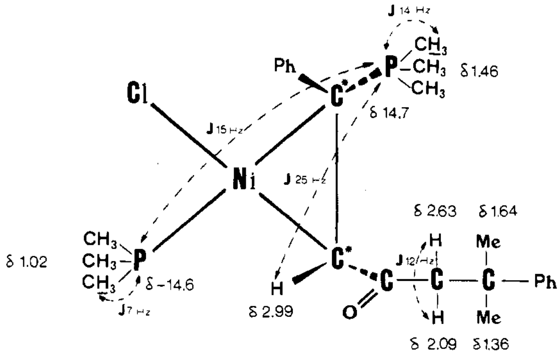
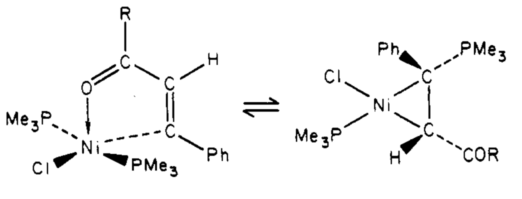


Figure 3. ^{1}H and ^{31}P NMR data for complex **2**.

In solution, complex **1d** exhibits the remarkable property of undergoing an unusual[10] and reversible 1,2 phosphine shift from the nickel atom onto the vinyl α-C atom, with spontaneous rearrangement to the nickelacyclopropane complex[11] $\overline{\text{Ni[C(Ph)(PMe}_3\text{)C}}$(H)(COCH$_2CMe_2$Ph)]Cl(PMe$_3$), **2**, containing a novel ylide ligand acting as a three-electron donor. The molecular complexity and bonding mode of this compound were determined by X-ray crystallography.[12]

Scheme I



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[8] Single crystals of **1b** were obtained from diethyl ether. Crystal data for complex **1b** are as follows: C$_{19}$H$_{35}$ClNiOP$_2$Si; M_r = 463.7; monoclinic; space group $P2_1/n$; a = 12.532 (8) Å, b = 14.099 (1) Å, c = 14.36 (1) Å, β = 98.51 (6)°, V = 2509 Å^3; ρ_{calcd} = 1.23 g cm^{-3}, Z = 4, $F(000)$ = 984; μ (Mo Kα) = 10.61 cm^{-1}. Intensity data collected on an Enraf-Nonius CAD-4F diffractometer using the ω–2θ scan technique; 2663 independent reflections measured in a quadrant, with $0 < \theta < 25°$; 1958 reflections considered observed $I \geq 3\sigma(I)$ after data reduction. Structure solved by Patterson and Fourier techniques and refined by least-squares methods. The methyl carbon atoms attached to P(1), P(2), and Si were considered isotropic, and the hydrogen atoms were geometrically placed and included in the refinement with fixed contributions, except H(31), whose coordinates were taken from a Fourier difference map and refined. The final R value (unit weights) was 0.056. All computations during data reduction and structure solution and refinement were carried out with the XRAY system.

[9] (a) Booth, B. L.; Hargreaves, R. G. *J. Chem. Soc. A* **1970**, 308. (b) Davidson, J. L.; Green, M.; Nyathi, J. Z.; Scott, C.; Stone, F. G. A.; Welch, A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1976**, 714.

[10] Scordia, H.; Kergoat, R.; Kubicki, M. M.; Guerchais, J. E.; L'Haridon, P. *Organometallics* **1983**, *2*, 1681.

[11] The compound NiCl(COCH$_2$CMe$_2$Ph)(PMe$_3$)$_2$ (0.4 g, 1 mmol) was treated with PhC≡CH as above.[6] The mixture was evaporated to dryness and the residue extracted with 70–80 mL of Et$_2$O. The resulting red-purple solution was centrifuged and kept at −30 °C overnight. Dark violet crystals of **2** were obtained, and they were filtered, washed with petroleum ether, and dried in vacuo. Evaporation of the red mother liquor to ca 5 mL and cooling at −30 °C furnished red crystals of isomer **1d**.

As shown in Figure 2, the nickel atom is in a trigonal environment, and the bonding in the nickelacyclopropane unit is slightly unsymmetrical, with the Ni–C(2) distance being somewhat shorter than the Ni–C(1) distance. The α twist of the C(1)–C(2) bond, measured[13] as the angle between the C(1)–C(2) line and the NiClP(1) plane is 8.5 (7)°, so that C(1) and C(2) deviate by 0.05 and 0.26 Å, respectively, from the mean least-squares coordination plane of the nickel atom. As expected the ylidic P(2)–C(2) distance at 1.77 (1) Å is appreciably shorter than the average P(2)–Me bond length (1.81 (2) Å). Conversion of **2** to its isomer **1d** is sufficiently slow to allow detailed NMR studies to be carried out. The results of these studies, which are summarized in Figure 3, conclusively show that the solid-state structure of this compound is maintained in solution.[14]

Work is now in progress to clarify the mechanism of this unusual rearrangement and to ascertain the potential role of **2** and of the other related species as intermediates in alkyne transformations induced by transition-metal complexes.

Acknowledgment. We thank the Spanish C.A.I.C.Y.T. for support of this work. We gratefully acknowledge Dr. David Cole-Hamilton (University of Liverpool) for recording high-field ^{1}H and ^{31}P NMR spectra.

Supplementary Material Available: Tables of crystal data, atomic coordinates, bond distances and angles, and thermal parameters for **1b** and **2** (12 pages). Ordering information is given on any current masthead page.

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(12) Crystal data: $C_{25}ClH_{37}NiOP_2$; M_r = 509.7; orthorhombic; space group *Pbca*; a = 20.638 (5) Å, b = 20.09 (1) Å, c = 12.913 (5) Å; V = 53 54 Å^3; D_{calcd} = 1.26 g cm^{-3}; Z = 8; $F(000)$ = 2160; μ(Mo Kα) = 9.59 cm^{-1}. Diffraction intensity data were collected on an Enraf-Nonius CAD-4F diffractometer using the ω–2θ scan technique. Of the 4669 reflections measured in an octant out to 2θ = 40°, 1277 unique reflections were considered observed ($I \geq 3\sigma(I)$). The structure was solved by Patterson and Fourier techniques and refined by least squares to an R value of 5.6%. The carbon atoms were considered isotropic. The hydrogen atoms were geometrically placed and included with fixed contributions in the refinement cycles, except H(1) whose coordinates, taken from a Fourier difference map, were refined.

(13) See for instance; Jolly, P. W. In "Comprehensive Organometallic Chemistry", Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: Oxford, 1982, Vol. 6, Chapter 37.5 and references therein.

(14) The assignment has been confirmed by selective decoupling experiments. The spectra were recorded in C_6D_6, at 250 MHz (^{1}H) and at 101.2 MHz (^{31}P). IR (Nujol mull, cm^{-1}): 1600 (ν(CO)). Anal. Calcd for $C_{25}H_{37}OP_2ClNi$: C, 58.9; H, 7.3. Found: C, 57; H, 7.3.

Reaction Energetics of a Dissociative Olefin Metathesis Mechanism for Dichlorotitanacyclobutane

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Received April 30, 1984

Summary: We have studied the rearrangement of dichlorotitanacyclobutane to the corresponding (olefin)titanium methylidene complex, characterizing in detail the wave functions, geometries, and energetics of each complex and the transition state connecting them. We find that the metallacycle is more stable than the olefin alkylidene complex by 11.5 kcal/mol and that there is no activation barrier for the rearrangement. We have further determined the olefin coordination energy to be 10.4 kcal/mol. From straightforward kinetic arguments we conclude that metathesis of the dichlorotitanacyclobutane complex, proceeding via a dissociative mechanism, should have an activiation enthalpy of 21.9 kcal/mol.

Olefin metathesis[1] is a transition-metal-assisted reaction that occurs quite easily with early transition metals. For example the Arrhenius activation energy for this reaction has been measured[1a] to be as low as 6.6 kcal/mol. The generally accepted mechanism for olefin metathesis[1] involves the reaction of a metal alkylidene with an olefin to form a metallacyclobutane that then decomposes to generate a new olefin and a new alkylidene complex. If the metal–carbon π bond is considered to be at least partially covalent, then this is a thermal 2 + 2 reaction, predicted to be "forbidden" by orbital symmetry rules.[2]

In this study we consider the isomerization of the parent dichlorotitanacyclobutane to form an ethylenetitanium methylidene complex. Previous work[3] has shown this chloride system to be a reasonable structural and energetic model of dicyclopentadienyltitanacyclobutane, a moderately active olefin metathesis catalyst.[4] We present calculations[5] characterizing the initial metallacycle and the final olefin methylidene complex as well as the transition state connecting them, demonstrating this reaction to have a very low barrier.

The geometry of the metallacycle is shown schematically in Figure 1a. The carbon–carbon bond distances (1.57 Å) are comparable to typical aliphatic carbon–carbon distances. The configuration at C_2 is nearly tetrahedral, but there are substantial departures from tetrahedral configurations at C_1 and C_3, with extremely small skeletal angles of 88.1°. The cyclopentadienyl analogue of this metallacycle, dicyclopentadienyltitanacyclobutane, displays a similar arrangement of bond lengths and angles at the carbon atoms.[4b] Our calculated Ti–C bond lengths of 2.12 Å are also in good agreement with the observed 2.15 Å. The bonding interactions are as discussed previously.[3a]

The product olefin methylidene complex is shown schematically in Figure 1c. The dichlorotitanium methylidene moiety is only weakly perturbed by the presence of the olefin from the configuration found previously to be optimum for the isolated alkylidene complex.[3a] Principle differences arise from steric interactions between the chloride ligands and the olefin, as the chlorides bend substantially out of the titanium–methylidene plane. The olefin seeks to reduce its interaction with the methylene group, and assumes an assymetric orientation, with the Ti–C_2 distance 0.1 Å greater than the Ti–C_3 distance. Similarly, the angle subtended by the C_1–Ti axis and the

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