was reduced in volume to ca. 4 mL. The solution was held at −20 °C overnight, and the pale yellow crystals that formed were isolated by filtration, washed with diethyl ether (ca 2 mL), and dried in vacuo: yield 113 mg (0.31 mmol, 55%); mp (sealed tube) 114 °C; IR (ν_{CO}, cyclohexane) 1978 cm^{-1}. Anal. Calcd for $IrC_{12}H_{11}O$: C, 39.66; H, 3.19. Found: C, 39.65; H, 3.19.

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Supplementary Material Available: ^1H NMR spectra of **1a** and **1b** (Figures 3 and 4), a comparison of observed and calculated ethylene regions of the ^1H NMR spectra of **1b** at the slow-exchange limit (Figure 5), and observed and calculated ethylene resonances for **1a,b** and **2a** from variable-temperature ^1H NMR studies (Figures 6–8) (6 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of a Carbon Suboxide Complex of Nickel, $(PPh_3)_2Ni(C,C'\text{:}\eta^2\text{-}C_3O_2)$

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Summary: Carbon suboxide reacts with $(PPh_3)_2Ni(C_8H_{12})$ in cold Et_2O to afford $(PPh_3)_2Ni(C,C'\text{:}\eta^2\text{-}C_3O_2)$ (**1**) as a yellow-green precipitate in 85% yield. Although **1** decomposes to nickel carbonyl products on dissolution in hydrocarbon solvents, it has been characterized by solid-state IR (ν(CO) = 1773, ν(CCO) = 2086 cm^{-1}) and multinuclear (^{13}C, ^{31}P) CP-MAS solid-state NMR spectroscopic techniques. The spectroscopic data for **1** and the isotopomers made from $O{=}^{13}C{=}C{=}^{13}C{=}O$ and $O{=}C{=}^{13}C{=}C{=}O$ show that the carbon suboxide ligand is bound to nickel in an η^2-olefin-like fashion through two carbon atoms.

During the course of our studies of the organometallic reaction chemistry of carbon suboxide (O=C=C=C=O), we have reported on the reactivity of C_3O_2 as a source of ligated "C" and "C_2O" fragments[1,2] and on 1,2-insertion reactions of C_3O_2 with transition-metal hydrides that yield formylketene ligands.[3] We also have an interest in exploring the simple coordination chemistry of the C_3O_2 molecule. However, as we and others[4] have observed, coordinatively unsaturated organometallic complexes normally react with C_3O_2 to extrude carbon monoxide to give the corresponding metal carbonyl derivatives, and this has generally frustrated attempts to prepare stable C_3O_2 complexes. Paiaro and co-workers have reported that $(PPh_3)_2Pt(C_2H_4)$ reacts with C_3O_2 to yield $(PPh_3)_2Pt(C_3O_2)$[5,6] and $[(PPh_3)_2Pt]_2(C_3O_2)$[6] as solid precipitates, the characterizations of which relied primarily on solid-state IR spectroscopy and elemental analyses because of the propensity for these complexes to rapidly decompose in solution via CO extrusion.

We report here that $(PPh_3)_2Ni(COD)$ (COD = 1,4-cyclooctadiene), prepared in situ by the addition of 2 equiv of PPh_3 to an Et_2O solution of $Ni(COD)_2$, reacts at −25 °C with a stoichiometric amount of C_3O_2 to afford $(PPh_3)_2Ni(C,C'\text{:}\eta^2\text{-}C_3O_2)$ (**1**) as an analytically pure, yellow–green precipitate in 85% yield (eq 1). This new coordination complex of carbon suboxide exhibits strong infrared absorptions at 2086 and 1773 cm^{-1} (Fluorolube mull) attributable to ν(CCO) and ν(CO), respectively.[7]

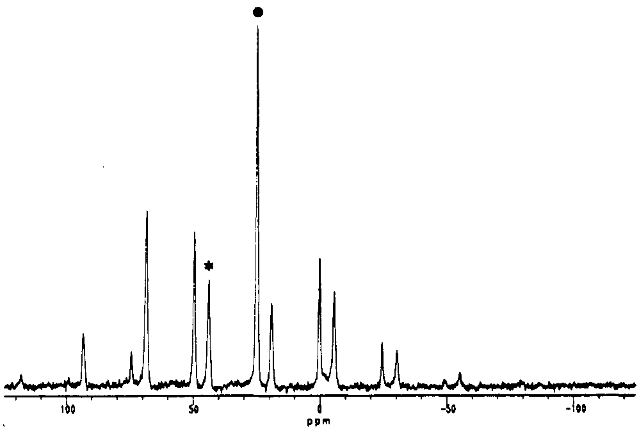

Figure 1. Solid-state CP-MAS $^{31}P\{^1H\}$ NMR spectrum of **1**. The isotropic chemical shift positions are labeled with asterisks. Integrated intensities include the central resonances and their sidebands.

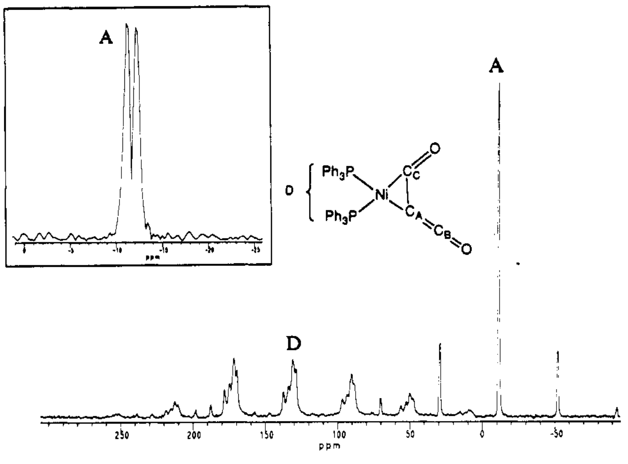

Figure 2. Solid-state CP-MAS $^{13}C\{^1H\}$ NMR spectrum of $1\text{-}^{13}C_1$ (20% isotopically enriched). The isotropic chemical shift positions are labeled with capital letters. The inset shows the resolution-enhanced resonance.

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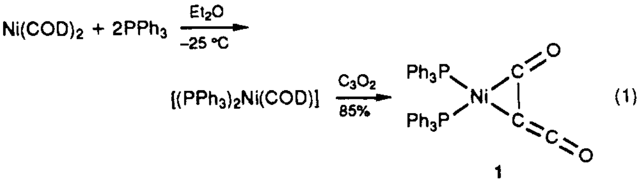

Two resonances (δ 24.8, 43.6; 1:1 integrated intensity) are observed in the solid-state CP-MAS $^{31}P\{^1H\}$ NMR spectrum of **1**, consistent with inequivalent, cis-disposed phosphine ligands bound to the square-planar Ni center, but because of the broadness of the resonances ($\sim$100 Hz, FWHM) the $^2J_{PP}$ was not observed (see Figure 1).

The CP-MAS $^{13}C\{^1H\}$ NMR spectra of **1**-$^{13}C_1$ (prepared from isotopically enriched O=C=^{13}C=C=O; Figure 2); and **1**-$^{13}C_2$ (prepared from isotopically enriched O=^{13}C=C=^{13}C=O; Figure 3) allow for assignment of the binding mode of the carbon suboxide ligand to Ni as C,C′:η^2-C_3O_2. The solution ^{13}C NMR spectrum of C_3O_2 (−40 °C, $CDCl_3$) exhibits resonances at δ −14.62 and +129.74 for the central and terminal carbon atoms, respectively.[8] Surprisingly, these resonances are only modestly perturbed upon coordination to the $Ni(PPh_3)_2$ center. In **1**-$^{13}C_1$, the enhanced resonance appears as a poorly resolved doublet (confirmed by resolution enhancement; see the Experimental Section) at δ −12.3 ($^2J_{CP}$ $\sim$ 16 Hz), indicating that the central C atom is attached to Ni (Figure 2). **1**-$^{13}C_2$ exhibits two enhanced resonances at δ 157.7 and 187.8, and resolution enhancement confirmed the multiplicities of the resonances to be that of a singlet and a doublet, respectively, indicating the latter resonance arises from the C atom bound to Ni (Figure 3). The broad line width of the resonance at δ 187.8 (88 Hz, FWHM) coupled with the low digital resolution of the spectrum (see the Experimental Section) precludes our obtaining an accurate J_{CP} for this doublet. The phosphine aryl resonances appear as multiplets at δ 130–138 in the spectra of both **1**-$^{13}C_1$ and **1**-$^{13}C_2$.

Although **1** is stable for days at room temperature in the solid state, hydrocarbon solutions (C_6H_6, C_7H_8, CH_2Cl_2) of **1** rapidly decompose to give an insoluble dark precipitate and, initially, $(PPh_3)_2Ni(CO)_2$ (IR, ^{31}P NMR). The fate of the "lost C atom" has not been ascertained. Finally, we were unable to prepare analogues of **1** with other phosphines and diphosphines, apparently owing to the facility with which the initially formed C_3O_2 adducts undergo CO extrusion, consistent with the findings of others that $\{P(c\text{-}C_6H_{11})_3\}_2Ni(COD)$ reacts with carbon suboxide to afford $\{P(c\text{-}C_6H_{11})_3\}_2Ni(CO)_2$.[4]

Experimental Section

Compounds were handled in an inert-atmosphere glovebox, and reactions were carried out by using standard high-vacuum and Schlenk techniques with dry, oxygen-free solvents.[9] Carbon suboxide was prepared by the dehydration of malonic acid, according to the method of Diels, and stored as a liquid at −78 °C in the dark.[10] Carbon suboxide specifically labeled with ^{13}C at the central or terminal carbon positions (O=C=^{13}C=C=O or O=^{13}C=C=^{13}C=O) was prepared from commercially available malonic-*2*-^{13}*C* acid (99 atom %, Sigma) or malonic-*1,3*-$^{13}C_2$ acid (99 atom %, Cambridge Isotope Laboratories) diluted to 20 atom % enrichment prior to dehydration. $Ni(COD)_2$ was used as purchased (Strem Chemicals). Solid-state infrared data (Fluorolube-S30 mulls, CaF_2 plates) were measured by using a Nicolet 20SXB instrument. Elemental analyses were performed by Desert Analytics (Tucson, AZ).

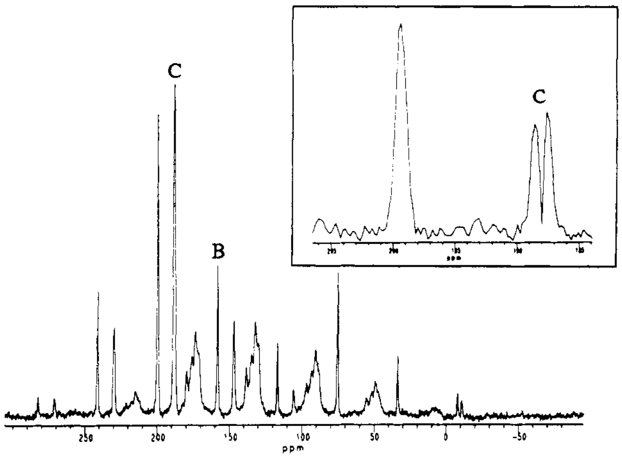

Figure 3. Solid-state CP-MAS $^{13}C\{^1H\}$ NMR spectrum of **1**-$^{13}C_2$ (20% isotopically enriched). The isotropic chemical shift positions are labeled with capital letters, and assignments refer to the labeling scheme shown in Figure 2. The inset shows the resolution-enhanced resonances.

Solid-state NMR spectra were recorded on a GE Omega-300 instrument equipped with a Chem-Magnetics solid-state NMR assembly. Samples were loaded in Kel-F rotors, and spectra were recorded at two different spin rates (3.1 and 2.8 kHz) to distinguish isotropic chemical shifts from spinning sidebands. $^{31}P\{^1H\}$ cross-polarization MAS spectra were obtained at 121 MHz with a 1-s recycle time and a 1-ms CP contact and were referenced to external 85% H_3PO_4 (δ 0). $^{13}C\{^1H\}$ cross-polarization MAS spectra were recorded at 75 MHz with a 4-s recycle time and a 2.5-ms CP contact and were referenced to an external Delrin rotor resonance (δ 88.0). In both ^{13}C and ^{31}P spectra, data (2 K real data points) were accumulated over a 30-kHz spectral width, giving a digital resolution of about 15 Hz. Resolution enhancement of the poorly resolved couplings in the ^{13}C NMR spectra was accomplished by applying a Gaussian multiplication followed by a $\sin^2$ multiplication to the FID.

Preparation of $(PPh_3)_2Ni(C,C'\text{:}\eta^2\text{-}C_3O_2)$ (1). A 25-mL flask was loaded with 322 mg (1.17 mmol) of $Ni(COD)_2$ and 314 mg (2.34 mmol) of PPh_3 and attached to a swivel-frit assembly. Diethyl ether (5 mL) was condensed onto the solids, the red-orange suspension was stirred at −78 °C for 1 h, and then C_3O_2 (1.30 mmol) was condensed onto the suspension from a calibrated volume. The resulting mixture was warmed to −25 °C and stirred for another 15 min, by which time the suspension had turned yellow in color. The suspension was filtered while cold and washed once with Et_2O (2 mL) to yield 647 mg (85%) of yellow-green powder. Anal. Calcd for $C_{39}H_{30}NiO_2P_2$: C, 71.92; H, 4.64. Found: C, 71.83; H, 4.40. IR: ν(CO) = 1773 (s), ν(CCO) = 2086 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (CP/MAS): δ 24.8 (s), 43.6 (s). ^{13}C NMR (CP/MAS; assignments were made with the use of the specifically ^{13}C-labeled derivatives prepared analogously to **1**; see Figures 2 and 3): δ −12.3 (d, NiC(O)*C*=C=O), 130–138 (mult, P*Ph*$_3$), 157.7 (s, NiC(O)C=*C*=O), 187.8 (d, Ni*C*(O)C=C=O).

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