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Articles

CO and Ethylene Migratory Insertion Reactions and Copolymerization Involving Palladium Complexes of a NiN_2S_2 Metallodithiolate Ligand

Marilyn V. Rampersad, Erik Zuidema, Jan Meine Ernsting,
Piet W. N. M. van Leeuwen,* and Marcetta Y. Darensbourg*[†]

Department of Chemistry, Texas A&M University, College Station, Texas 77843, and
Anorganisch Chemisch Laboratorium, J. H. van't Hoff Research Institute,
Universiteit van Amsterdam, van't Hoff Institute for Molecular Sciences,
Nieuwe Achtergracht 166, NL 1018 WV Amsterdam, The Netherlands

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Neutral ((**Ni-1**)$Pd(CH_3)(Cl)$) and cationic ([(**Ni-1**)$Pd(CH_3)(OEt_2)$][BAr'_4]) complexes containing the strongly electron-donating metallodithiolate ligand **Ni-1** ([(*N*,*N*′-bis(2-mercaptoethyl)-*N*,*N*′-diazacyclooctane]nickel(II), ($S(CH_2)_2N((CH_2)_3)_2N(CH_2)_2S$)Ni) have been prepared. Carbonylation reactions with these Pd−alkyl complexes were investigated by IR and high-pressure NMR spectroscopy. Carbon-13 NMR spectroscopic studies showed that the rates of CO insertion to form the derivatives (**Ni-1**)$Pd(C(O)CH_3)(Cl)$ and $[($**Ni-1**$)Pd(C(O)CH_3)(CO)]^+$ were immeasurably fast at −80 °C in CD_2Cl_2, in contrast to slower rates for Pd metal based diphosphine and diimine analogues. It was further shown that displacement of the terminally bound CO by ethylene in the acetylated derivative $[($**Ni-1**$)Pd(C(O)CH_3)(CO)]^+$ was slow, attributable to the high binding affinity of CO toward Pd^{2+} in the presence of the electron-rich nickel dithiolate ligand. Bulk copolymerization studies of CO/ethylene in the presence of the cationic catalyst precursor [(**Ni-1**)$Pd(CH_3)(OEt_2)$][BAr'_4] find alternating polyketones. The catalytic efficiency is solvent-dependent: $CH_2Cl_2 > CH_3CN > THF$. From low-pressure and bulk copolymerization studies the resting state of the catalyst was determined to be the open-chain intermediate $[($**Ni-1**$)Pd(C(O)R)(CO)]^+$ rather than the β- and γ-keto chelate complexes $[(L^\frown L)Pd(CH_2CH_2(O)R_3)]^+$ and $[(L^\frown L)Pd(C(O)CH_2CH_2(O)R_3)]^+$ that were found for diimines and diphosphines.

Introduction

The efficacy of a catalyst depends on the metal as well as the surrounding ligands, which provide the steric and electronic environment necessary to influence catalyst performance in terms of rate and selectivity.[1−2] Therefore, important technological advances in biomimetic or industrial catalyst development and modification rely on a fundamental understanding of the ligand properties and their effects on the metal center during catalysis.[1−4]

Inspired by a heterobimetallic biological catalyst, acetyl CoA synthase (ACS), we have endeavored to develop *cis*-dithiolato NiN_2S_2 metal complexes as a new class of ligands for organometallic chemistry.[5−8] The active site of the ACS enzyme contains a Cys-Gly-Cys motif which binds nickel(II) in an N_2S_2 diamido, dithiolato square plane. The $NiN_2S_2^{2-}$ complex is coordinated through the sulfurs to a second nickel which is catalytically active in sequential C−C and C−S coupling reactions.[8−9] This natural NiN_2S_2 ligand joins a collection of synthetic analogues which have distinctive steric, electronic, and structural properties, as established through derivatives of tungsten tetracarbonyl.[10] These ligands may be neutral NiN_2S_2 or dianionic $NiN_2S_2^{2-}$ donors, both of which were found to be better electron-donating ligands than classical diphosphines, diimines, and dithioether ligands. They have a unique stereochemical orientation with respect to the coordinated metal, as shown in Figure 1 for the heterobimetallic complex (**Ni-1**)Pd-

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[†] Fax: (979) 845-0158. E-mail: marcetta@mail.chem.tamu.edu.

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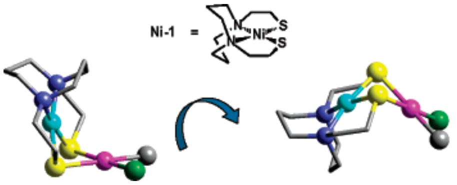
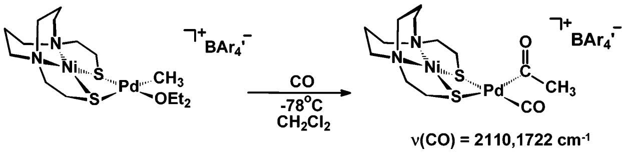


Figure 1. Butterfly core defined by the (μ-SR)$_2$ bridge or hinge in (**Ni-1**)Pd(CH$_3$)(Cl).

(CH$_3$)(Cl).[10,11] This unique "hinge-angle" or "butterfly" feature might allow for stereo- and regioselective substrate addition.

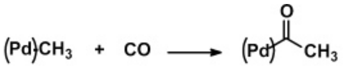
The μ-SR bridge feature formed between the NiN$_2$S$_2$ chelate and a Pd^{2+} metal center, displayed in the two views in Figure 1, is a direct analogue of the dinickel active site in ACS.[5−7] An added functionality of metallodithiolate ligands is their ability to serve as hemilabile ligands.[12] Bond dissociation between sulfur and the catalytic metal provides an open site on an otherwise coordinatively saturated metal center. Hemilability may also account for stabilization of the catalytically active metal during oxidation state changes which require different coordination numbers.

The heterobimetallic complex (**Ni-1**)Pd(CH$_3$)(Cl) (Figure 1) was designed to mimic structural and functional features of the ACS enzyme active site as well as to serve as a catalyst or catalyst precursor in a probe reaction in C−C coupling reactions, specifically CO/olefin copolymerization.[11] Elegant mechanistic studies by Sen,[13−15] Brookhart,[16] Drent,[17] and van Leeuwen[18] over the past decade have provided substantial mechanistic information that highlighted the key steps of CO/ethylene chemistry and delineated the formation of perfectly alternating polyketone (Figure 2), as catalyzed by amine and phosphine derivatives of Pd$^{\text{II}}$. By analogy we expect that the NiN$_2$S$_2$ ligand might take the place of a diphosphine or diimine ligand. In preliminary studies this analogy was demonstrated for the methyl migration/CO insertion reaction given in eq 1.[11]

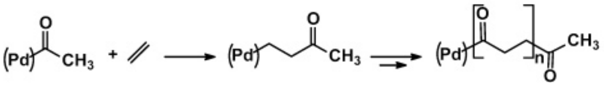


(1)

In CO/olefin copolymer catalysis the migratory insertion of CO into a Pd−alkyl bond (eq 2) is followed by ethylene binding and migratory insertion into a Pd−acetyl bond (eq 3).[2,15,19] Sen et al. have shown that double CO insertion is thermodynamically unfavorable and that double insertion of ethylene is retarded by the high affinity of Pd$^{\text{II}}$ metal centers for CO.[13−15]



$$(\text{Pd})\text{CH}_3 + \text{CO} \longrightarrow (\text{Pd})\text{C(O)CH}_3 \quad (2)$$



$$(\text{Pd})\text{C(O)CH}_3 + \text{C}_2\text{H}_4 \longrightarrow (\text{Pd})\text{CH}_2\text{CH}_2\text{C(O)CH}_3 \longrightarrow (\text{Pd})[\text{C(O)CH}_2\text{CH}_2]_n\text{C(O)CH}_3 \quad (3)$$

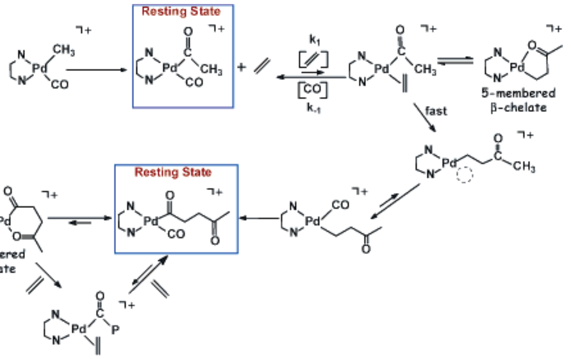


Figure 2. Mechanism proposed by Brookhart et al. for the copolymerization of CO/C$_2$H$_4$ employing palladium diimine catalysts.[16]

Ligand effects on this reaction have been explored with a variety of diphosphines and diimines. With the diphosphine complex [(dppp)Pd(CH$_3$)][OTf]$^-$ (dppp = bis(diphenylphosphino)propane), Drent and co-workers found evidence that the resting states of the catalysts under mild conditions are the α,β-keto chelate complexes.[17] They suggested that CO replacement of the O donor in the γ-keto chelate reduces steric crowding, facilitates the side-on approach of ethylene, and results in more facile CO/C$_2$H$_4$ exchange and C$_2$H$_4$ insertion.[17] In contrast, Brookhart and co-workers posited that the relatively flat phenanthroline ligand provided less steric crowding and facilitated the direct ketone displacement by ethylene.[16] Thus, in this case the resting state of the catalyst is the open-chain acetyl carbonyl [(o-phen)Pd(C(O)R)(CO)]$^+$, attributable to the much larger binding affinity of CO over ethylene for the metal center (Figure 2).

In addition to the ligand dependence of resting states of the catalyst during CO/C$_2$H$_4$ copolymer formation, there exist differences between the mechanistic route to CO addition in neutral (L$_2$)Pd(CH$_3$)(X) and cationic [(L$_2$)Pd(CH$_3$)]$^+$[X]$^-$ metal complexes.[17,18] These differences may derive from the ligand's steric and electronic components as well as the charge and coordination geometry of the overall complex.[18] In order to place the NiN$_2$S$_2$ ligands more clearly in the scheme of such a catalytically significant reaction, high-pressure ^{13}C NMR studies were conducted in order to monitor the carbonylation reaction of the neutral (**Ni-1**)Pd(CH$_3$)(X) and [(**Ni-1**)Pd(CH$_3$)]$^+$[X]$^-$ metal complexes. As it relates to CO/olefin copolymerization, the reactivity of the acetylated derivative [(**Ni-1**)Pd(C(O)CH$_3$)(CO)]$^+$ with ethylene is also described along with preliminary results regarding the catalytic activity of [(**Ni-1**)Pd(CH$_3$)(OEt$_2$)]$^+$ in the CO/ethylene copolymerization reaction with varying ethylene concentrations and solvents. With these results, the nickel dithiolate ligand is compared to the classical L$_2$ ligands.

Experimental Section

Definitions: cod = cyclooctadiene, HBAr′$_4$ = [H(OEt$_2$)$_2$][(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$B], TMEDA = tetramethylethylenediamine, **Ni-1** = (N,N'-bis(2-mercaptoethyl)-N,N'-diazacyclooctane)nickel(II).

General Methods and Materials. All manipulations were performed on a double-manifold Schlenk vacuum line under an

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atmosphere of nitrogen or in an argon-filled glovebox. Solvents were reagent grade and were predried and deoxygenated according to published procedures under a N_2 atmosphere.[20] The complexes (TMEDA)Pd$(CH_3)_2$,[21] H$(OEt_2)_2$BAr$'_4$,[22] (cod)Pd(CH_3)(Cl),[23] **Ni-1**,[24] and (**Ni-1**)Pd$(CH_3)_2$[11] were synthesized according to published procedures. All other chemicals were purchased from Aldrich Chemical Co. and used as received. All compounds were stored under an argon atmosphere at −45 °C. The CO gas used was filtered through a Drierite column before use.

Physical Measurements. Canadian Microanalytical Services, Ltd., Delta, British Columbia, Canada, performed elemental analyses. Mass spectral analyses were done at the Laboratory for Biological Mass Spectroscopy at Texas A&M University. Electrospray ionization mass spectra were recorded using an MDS-Series QStar Pulsar instrument with a spray voltage of 5 eV. MALDI-TOF measurements were performed on an ABI Voyager-DE STR spectrometer, operating in positive reflection mode. Dithranol (1,8,9-trihydroxyanthracene) was used as the matrix, and the polymer was dissolved in hexafluoro-2-propanol ($(CF_3)_2CHOH$. Note that $(CF_3)_2CHOH$ is a highly toxic and corrosive solvent that is destructive to tissues, membranes, eyes, skin, and respiratory tract and should be used with extreme care). Infrared spectra were recorded on a Bruker Optics 6021 FTIR spectrometer with a DTGS detector. ^{13}C NMR studies were carried out on an INOVA 500 MHz Varian spectrometer with a 1 cm high-pressure sapphire NMR tube. N.B.: care must be taken to ensure there are no scratches or microfractures on the tube, which may provide a nucleation point for explosion during pressurization. The tube was cleaned by consecutive rinsings with CH_2Cl_2 and by a gentle scrub using a modified pipe cleaner. Visible/UV spectra were recorded in CH_2Cl_2 on a Hewlett-Packard HP8552A diode array spectrometer. ^{13}C NMR analysis of the polyketone was carried out with an INOVA 400 MHz Varian spectrometer in a 1:1 mixture of $(CF_3)_2CHOH$ and $CDCl_3$.

Preparation of (NiN_2S_2)PdR_2 Complexes. (a) [(*N,N′*-Bis(2-mercaptoethyl)-*N,N′*-diazacyclooctane)nickel(II)]palladium(Methyl)(Diethyl Ether), [(Ni-1)Pd(CH_3)(OEt_2)][BAr′$_4$]. Under an argon atmosphere solids of the red (**Ni-1**)Pd$(CH_3)_2$ (0.030 g, 0.070 mmol) and white HBAr$'_4$ (0.071 g, 0.070 mmol) were added to a flame-dried and degassed Schlenk tube, which was immediately placed in a −30 °C dry ice/CH_3CN ice bath. A 3:1 v/v mixture of CH_2Cl_2 and diethyl ether was added to the solids, taking care to dissolve all of the reactants (CO exposure to unreacted (**Ni-1**)Pd$(CH_3)_2$ results in decomposition to Pd black). The orange-red solution was stirred for 2 h at −30 °C, followed by the evaporation of the solvent under vacuum to yield an orange-red solid, yield 0.068 g (72%). UV−vis (in CH_2Cl_2 solution; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 236 (24 710), 272 (15 770), 280 (15 435), 302 (9730), 330 (5830), 396 (1440), 518 (564). Mass spectrum (CH_3CN solution; *m/z* (% abundance relative to base peak at 100%)): 413 [(**Ni-1**)Pd$(CH_3)]^+$ (97%), 454 [(**Ni-1**)Pd$(CH_3)(CH_3CN)]^+$ (100%).

(b) [(*N,N′*-Bis(2-mercaptoethyl)-*N,N′*-diazacyclooctane)nickel(II)]palladium(Methyl)(Chloride), (Ni-1)Pd(CH_3)(Cl). Under N_2, 20 mL of CH_2Cl_2 was added to a degassed sample of (cod)Pd(CH_3)(Cl) (0.20 g, 0.75 mmol). To this colorless solution was added a purple solution of **Ni-1** (0.22 g, 0.75 mmol dissolved in 30 mL of CH_2Cl_2). The resulting red-pink solution was stirred for 5 h at room temperature before the solution was concentrated to about 5 mL, resulting in a red precipitate. The slurry was washed with pentane (2 × 20 mL) and then dried under vacuum to yield a red-pink solid of 0.32 g (80%) of (**Ni-1**)Pd(CH_3)(Cl)·CH_2Cl_2. (The CH_2Cl_2 solvent molecule was observed in the X-ray diffraction study.) Anal. Calcd (found) for $C_{12}H_{25}N_2S_2NiPdCl_3$: C, 26.2 (27.0); H, 4.94 (4.73); N, 5.86 (5.26). Included in the calculated elemental analysis is a CH_2Cl_2 solvent molecule that was observed in the X-ray diffraction study of the crystals. UV−vis (in CH_2Cl_2 solution; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 232 (18 010), 262 (13 810), 302 (8560), 526 (460). Mass spectrum (CH_3CN solution; *m/z* (% abundance relative to base peak at 100%)): 413 [(**Ni-1**)Pd$(CH_3)]^+$ (100%), 454 [(**Ni-1**)Pd$(CH_3)(CH_3CN)]^+$ (22%).

Preparation of [(*N,N′*-Bis(2-mercaptoethyl)-*N,N′*-diazacyclooctane)nickel(II)]palladium(Acetyl)(Chloride), (Ni-1)Pd(C(O)-CH_3)(Cl). Under argon, a sample of solid (**Ni-1**)Pd(CH_3)(Cl) (0.030 g, 0.066 mmol) was placed in a degassed and flame-dried Schlenk tube and cooled to −78 °C in a dry ice/acetone bath. Approximately 5 mL of CH_2Cl_2 was added to the flask, followed by vigorous sparging of CO gas for 5 min. The solution was stirred for an additional 30 min at −78 °C. IR (CH_2Cl_2; ν(C=O), cm^{-1}): 1692 (s). ^{13}C NMR (CD_2Cl_2; δ, ppm): 225 (s, C(O)).

Copolymerization of CO and Ethylene. Samples of (**Ni-1**)Pd$(CH_3)_2$ and HBAr$'_4$ were added to a flame-dried degassed vial, in which 15 mL of CH_2Cl_2 was added. The solution was cooled to −78 °C and stirred for 10 min before being transferred via an injection port to a stainless steel 300 mL Parr autoclave at room temperature. The autoclave was predried at 80 °C under vacuum for 8 h and cooled to room temperature prior to use. The vial was washed with an additional 10 mL of CH_2Cl_2, and the washings were added to the autoclave. The autoclave was charged with CO gas followed by ethylene; the contents were heated at the desired temperature for the designated time. Copolymerization was initiated at the time of monomer addition and was stopped by removing the autoclave from its heating mantle, thereby cooling to room temperature. The remaining gases were vented in the fume hood. The polymer was extracted from the catalyst by precipitation with an acidic methanol solution (95% CH_3OH and 5% concentrated HCl). The grayish to white polymer was collected via filtration, dried, and weighed. IR ($(CF_3)_2CHOH$; ν(C=O), cm^{-1}): 1704 (s). ^{13}C NMR (400 MHz, $(CF_3)_2CHOH/CDCl_3$, 25 °C; δ, ppm): 220.0 (s, C(O)), 43 (s, α-CH_2).

^{13}C NMR Study of CO Addition to [(Ni-1)Pd(CH_3)(OEt_2)][BAr′$_4$]. To a degassed flame-dried Schlenk tube was added [(**Ni-1**)Pd$(CH_3)(OEt_2)$][BAr$'_4$] (0.053 g, 0.039 mmol), to which 2 mL of anhydrous CD_2Cl_2 was added under Ar. The red solution was transferred via a plastic cannula into a high-pressure sapphire NMR tube that had been flushed with Ar for 15 min. With an Ar purge, the stainless steel cap was placed on the top of the tube simultaneously as the plastic cannula was removed. The sample was cooled to −80 °C in a dry ice/acetone bath and pressurized to a total of 8 bar with isotopically labeled ^{13}CO gas a few minutes prior to transporting the sample to the NMR spectrometer (probe precooled to −80 °C). Approximately 5 min after CO addition, the NMR tube was wiped dry on the outside, shaken once, and inserted into the precooled NMR instrument. Consecutive ^{13}C NMR spectra were recorded over the range −80 to +60 °C.

^{13}C NMR Study of CO Addition to (Ni-1)Pd(CH_3)(Cl). By a procedure almost identical with that for the preparation of [(**Ni-1**)Pd$(CH_3)(OEt_2)$][BAr$'_4$] for CO addition, the red-pink solid (**Ni-1**)Pd(CH_3)(Cl) (0.018 g, 0.040 mmol) was dissolved in 2 mL of anhydrous CD_2Cl_2 in a flame-dried degassed flask under an argon atmosphere. The 20 mM solution was transferred to the sapphire NMR tube (degassed thoroughly in a large Schlenk tube via vacuum and refilled with Ar at 1 bar), which was cooled to −80 °C and charged to 9 bar with isotopically labeled ^{13}CO gas a few minutes prior to transporting the sample to the NMR instrument (probe

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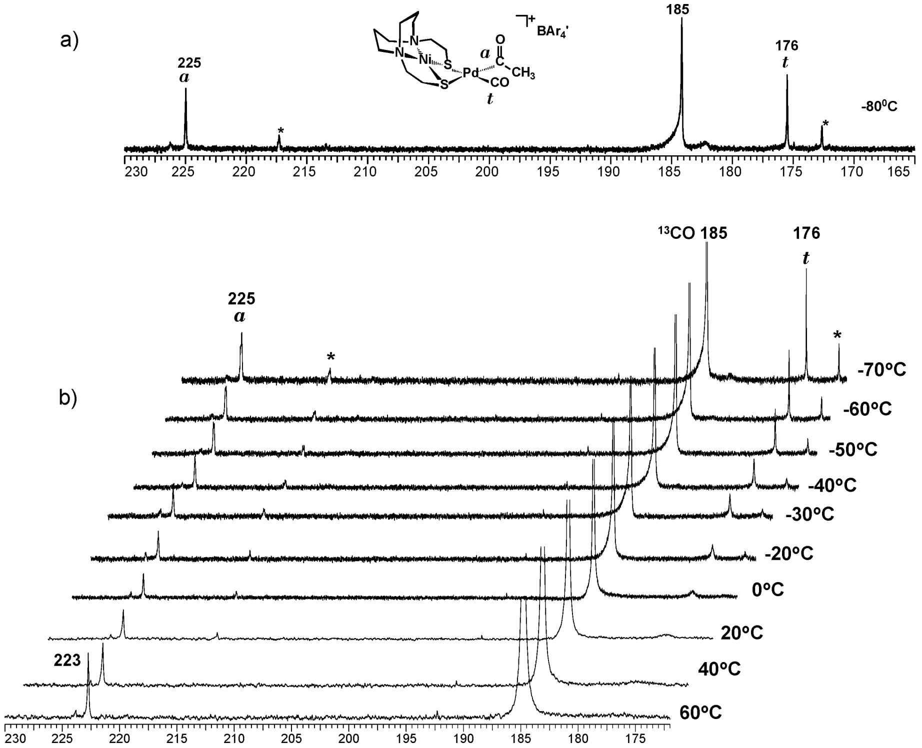


Figure 3. ^{13}C NMR study of CO uptake by the [(**Ni-1**)Pd(CH$_3$)(OEt$_2$)]$^+$ complex: (a) spectrum at −80 °C; (b) monitoring of the effect of raising the temperature from −70 to 60 °C in a high-pressure sapphire NMR tube at 7 bar of ^{13}CO. Asterisks indicate minor impurities.

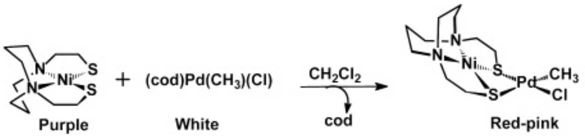
precooled to −80 °C) (N.B.: the total pressure in the tube is 9 bar (8 bar of CO + 1 bar of Ar)). Approximately 5 min after CO addition, the ^{13}C NMR spectra were recorded over the range −80 to +30 °C.

^{13}C NMR Study of CO and Ethylene Uptake by [(Ni-1)Pd(CH$_3$)(OEt$_2$)][BAr′$_4$]. A sample of [(**Ni-1**)Pd(CH$_3$)(OEt$_2$)][BAr′$_4$] (0.057 g, 0.042 mmol) dissolved in 2 mL of CD$_2$Cl$_2$ was prepared in a manner identical with that above. The 21 mM sample was pressurized with 7 bar of ^{13}CO gas approximately 5 min prior to recording the ^{13}C NMR spectrum at −80 °C (NMR instrument precooled to −80 °C). For the addition of ethylene, the NMR tube was depressurized to 1 bar in a fume hood and charged with 4 bar of ethylene at −80 °C in a dry ice/acetone bath (total pressure 5 bar). Consecutive ^{13}C NMR spectra were recorded over the range −80 to +20 °C.

Results and Discussion

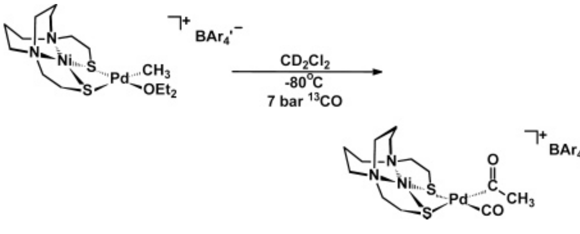
According to the experimental protocol laid out by Brookhart et al.,[16] the monomethyl derivative [(**Ni-1**)Pd(CH$_3$)(OEt$_2$)][BAr′$_4$] was prepared from (**Ni-1**)Pd(CH$_3$)$_2$ by the acid release of CH$_4$. This complex is an extremely useful precursor that is stable as a red solid at low temperature. Mass spectral analysis of the product dissolved in acetonitrile found that the base peak (100%) is the acetonitrile adduct [(**Ni-1**)Pd(CH$_3$)(CH$_3$CN)]$^+$, with a mass to charge ratio of 454. The stability of [(**Ni-1**)Pd(CH$_3$)(OEt$_2$)][BAr′$_4$] in CH$_2$Cl$_2$ solution was monitored by UV−vis spectroscopy at room temperature. Spectral changes of the d−d transitions were observed after 2 h, with more prominent changes occurring overnight, showing a dramatic increase in absorbance with a concurrent shift in the absorptions of the starting complex at 396 and 518 nm (orange-red) to 402 and 522 nm (opaque dark purple) (see the Supporting Information). These spectroscopic features are consistent with the formation of trimetallic complexes such as the dark purple [(**Ni-1**)$_2$Pd]$^{2+}$(Cl)$_2$ (λ_{max} at 408 (5245), 522 nm (3730 M^{-1} cm^{-1}) in CH$_3$OH) that has been spectroscopically and structurally characterized.[11] The trimetallic complex [**Ni-1**]$_2$Pd[BAr′$_4$]$_2$ and Pd^0 metal are products of a well-known thermal decomposition reaction of L$_2$Pd(CH$_3$)$_2$ complexes (L$_2$ = diimine) by release of ethane.[21] As a solid, the (**Ni-1**)Pd(CH$_3$)$_2$ complex is stable at low temperature.

Our original report of the (**Ni-1**)Pd(CH$_3$)Cl complex derived from the unplanned reactivity of (**Ni-1**)Pd(CH$_3$)$_2$ with CH$_2$Cl$_2$ solvent.[11] A direct and facile preparation of (**Ni-1**)Pd(CH$_3$)(Cl) in 95% yield was adopted from the method of van Leeuwen and co-workers by metallodithiolate ligand substitution of the cyclooctadiene in (cod)Pd(CH$_3$)(Cl) (eq 4).[23] Mass spectral analysis of the product in acetonitrile found that the base peak was [(**Ni-1**)Pd(CH$_3$)]$^+$ with a mass to charge ratio of 413, while at 22% the acetonitrile adduct [(**Ni-1**)Pd(CH$_3$)(CH$_3$CN)]$^+$ was seen.



(4)

^{13}C NMR Study of CO Addition to [(Ni-1)Pd(CH$_3$)(OEt$_2$)][BAr′$_4$]. In order to study the migratory insertion possibilities of [(**Ni-1**)Pd(CH$_3$)(OEt$_2$)]$^+$, a 20 mM sample of the complex as its [BAr′$_4$]$^-$ salt was prepared at room temperature, placed in a high-pressure sapphire NMR tube, and cooled to −80 °C prior to the addition of ^{13}CO gas to 7 bar (eq 5).



(5)

The ^{13}C NMR spectrum was recorded within 5 min of CO

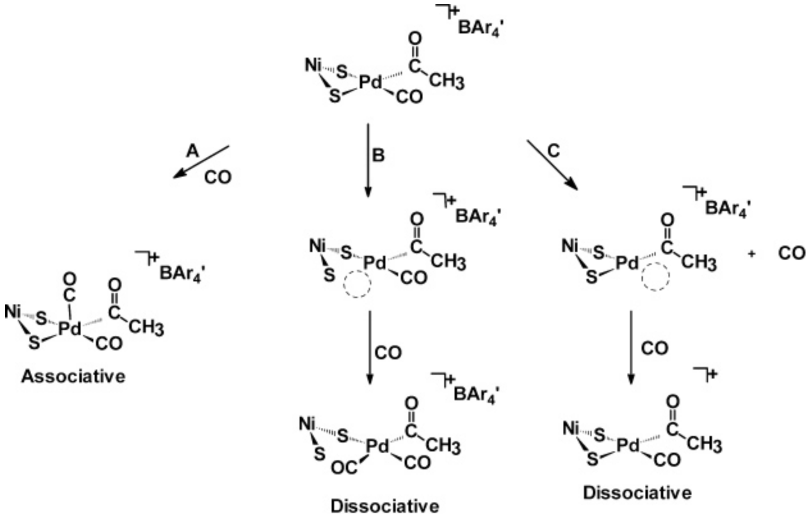


Figure 4. Possible reaction pathways for CO exchange in $[(\mathbf{Ni\text{-}1})Pd(C(O)CH_3)(CO)]^+$.

addition and transport of the sample to the NMR instrument that was precooled to −80 °C.

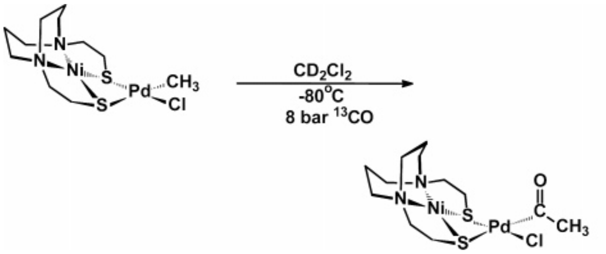
Carbon-13 NMR spectra were recorded at −80 °C and at 10 °C increments as the temperature was increased to 60 °C (Figure 3). At −80 °C the ^{13}C NMR spectrum displayed three sharp signals in the CO region (Figure 3a). The large resonance at 185 ppm is assigned to free ^{13}CO dissolved in CD_2Cl_2. The signal at 225 ppm is assigned to the carbonyl carbon of the acetyl group (CO_a), coordinated to the palladium metal center, while the resonance at 176 ppm, upfield from free ^{13}CO, is assigned to carbon of a terminally bound CO ligand (CO_t). Resonances with asterisks represent minor impurities. The assignments are in accord with that of the complex $[(o\text{-phen})Pd(C(O)CH_3)(CO)]^+$, reported by Brookhart and co-workers.[16]

When the sample was warmed, the resonance of the acetylated carbonyl derivative observed at −80 °C did not grow in intensity. This suggested that CO/CH_3^+ migratory insertion was complete within 5 min. The fast rate of CO reaction and insertion with $[(\mathbf{Ni\text{-}1})Pd(CH_3)(OEt_2)]^+$ at −80 °C thus prevented observation of the presumed intermediate, $[(L_2)Pd(CH_3)(CO)]^+$, which was observable with the diphosphine and diimine ligands. Quantitative studies with such ligands have determined rate constants for migratory insertion in a diphosphine derivative, $[(dppp)Pd(CH_3)(CO)]^+$ ($k_{obs} = 4.5 \times 10^{-5}$ s^{-1} ($\Delta G^\ddagger = 61.7(1)$ kJ/mol, −81.7 °C)), and in a diimine derivative, $[(o\text{-phen})Pd(CH_3)(CO)]^+$ ($k_{obs} = 2.5 \times 10^{-4}$ s^{-1} ($\Delta G^\ddagger = 64.5$ kJ/mol, −66 °C)).[16,20] Thus, it is evident that the rate of methyl migration on the palladium metal center is much more rapid in the presence of the metallodithiolate ligand as compared to the rate for the classical ligands in similar cationic complexes.

^{13}CO Exchange in $[(\mathbf{Ni\text{-}1})Pd(C(O)CH_3)(CO_t)]^+$. As shown in Figure 3b, as the sample of $[(\mathbf{Ni\text{-}1})Pd(C(O)CH_3)(CO_t)]^+$ in CD_2Cl_2 under ^{13}CO is warmed, the terminally bound CO_t resonance at 176 ppm disappears with concomitant broadening of the free ^{13}CO signal at 185 ppm. This observation is interpreted as ligand exchange between the terminally bound CO_t and free ^{13}CO dissolved in solution. Over the same temperature range the acetyl signal remains relatively sharp and only shows a slight upfield shift to 223 ppm.

Terminal CO_t exchange may occur via dissociative or associative pathways. Ligand dissociation via Ni−S or Pd−CO bond breaking (path B or C in Figure 4) would result in the formation of a 14-electron, open-site intermediate. Because of greater activation barriers to bond breaking, however, such processes are unlikely at low temperature. An associative pathway is expected to be the favored route to ligand exchange (path A), as it involves a five-coordinate, square-pyramidal, 18-electron intermediate species (Figure 4). This is similar to a ligand exchange process confirmed to be associative by Brookhart and co-workers, in which the alkyl carbonyl complex $(o\text{-phen})Pd(CH_3)(^{12}CO)$ underwent rapid exchange with ^{13}CO.[16]

^{13}C NMR Study of CO Addition to $(\mathbf{Ni\text{-}1})Pd(CH_3)(Cl)$. The same procedure as described above was applied to CO addition to the neutral complex $(\mathbf{Ni\text{-}1})Pd(CH_3)(Cl)$ (eq 6). A 20 mM sample was pressurized with 8 bar of isotopically labeled ^{13}CO gas at −80 °C, and the ^{13}C NMR spectrum was recorded in the precooled NMR spectrometer probe within 5 min after CO addition.



(6)

As shown in Figure 5a, the resonance for free ^{13}CO dissolved in solution is observed at 185 ppm and a signal at 226 ppm is assigned to the acetyl, CO_a. Notably, CO addition to similar neutral complexes of the type $L_2Pd(CH_3)(Cl)$ (L = diimine) also forms acetylated derivatives, $L_2Pd(C(O)CH_3)(Cl)$.[26] Consistently, the infrared spectrum of the acetylated $(\mathbf{Ni\text{-}1})Pd(C(O)CH_3)(Cl)$ shows a ν(C=O) stretch at 1692 cm^{-1}, in agreement with the ν(C=O) stretching frequency (1690 cm^{-1}) of the $(bipy)Pd(C(O)CH_3)(Cl)$ complex.[18]

When the solution was warmed from −70 to 20 °C, the C-13 resonance assigned to the carbon of the acetyl ligand did not intensify (Figure 5b). This signifies that CO addition to the neutral complex $(\mathbf{Ni\text{-}1})Pd(CH_3)(Cl)$ was complete at −80 °C within the same time frame as that of the cationic derivative $[(\mathbf{Ni\text{-}1})Pd(CH_3)(OEt_2)]^+$; i.e., we are unable to measure events that happen during the first 5 min from the time of mixing of CO and the NiPd derivatives. Interestingly, the rate

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[26] van Asselt, R.; Gielens, E. C. G.; Rülke, R. E.; Elsevier, C. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1203−1205.

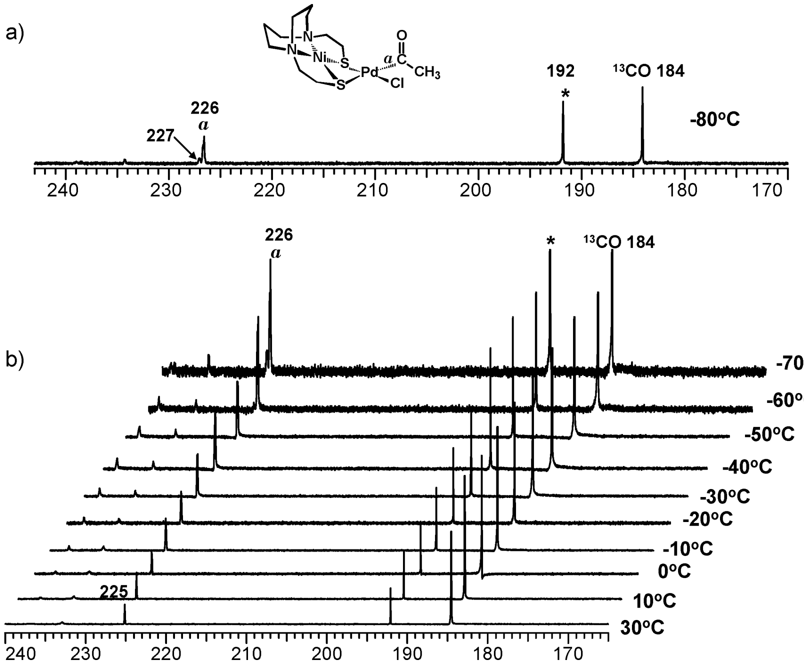

Figure 5. ^{13}C NMR spectra of CO uptake by (**Ni-1**)Pd(CH$_3$)(Cl): (a) spectrum at −80 °C; (b) monitoring of the effect of raising the temperature from −70 to 30 °C in a high-pressure sapphire NMR tube at 8 bar of ^{13}CO. Asterisks indicate Ni(CO)$_4$ impurity (see text).

of CO/CH$_3$ migratory insertion with the (bipy)Pd(CH$_3$)(Cl) complex is reported to be much slower: $k_r = 4.05 \times 10^{-4}$ s^{-1} at 20 °C.[18]

We have assigned the large resonance observed at 192 ppm to the carbonyl ligands of Ni(CO)$_4$,[27] an unfortunate impurity from a reaction between ^{13}CO gas trapped in a gas regulator composed of a nickel alloy. That the Ni(CO)$_4$ formation was not the result of a decomposition reaction formed by oxidation of the thiolate donors to form disulfide, reducing Ni^{2+} to Ni^0 in the presence of CO, was explored by the following experiment. Addition of ^{13}CO to the free metallodithiolate ligand over an extended period did not result in Ni(CO)$_4$ formation. The ^{13}C NMR spectrum of the sample after being depressurized of CO followed by a slight argon purge at 20 °C showed a significant decrease in the resonances for free ^{13}CO and Ni(CO)$_4$ dissolved in solution. The carbonyl acetyl signal, however, remained sharp and unchanged, further affirming that the (**Ni-1**)Pd(C(O)CH$_3$)(Cl) species does not undergo deinsertion and CO exchange. Other interesting features observed in the ^{13}C NMR spectra are a small resonance at 227 ppm and a slight line broadening of the acetyl signal that occurs as the temperature is raised. This will be addressed later.

Possible Mechanisms of CO Addition/Migratory Insertion to (Ni-1)Pd(CH$_3$)(Cl). The observation of an acetyl group within the neutral complex (**Ni-1**)Pd(C(O)CH$_3$)(Cl) raised questions regarding the CO addition reaction and the enhanced rate of migratory insertion as compared to the rate for (L$_2$)Pd(CH$_3$)(Cl) (L$_2$ = diimines). Dissociative routes involving the Cl$^-$ ion as proposed for (L$_2$)Pd(CH$_3$)(Cl) complexes are unlikely, since Cl$^-$ dissociation at such low temperatures (−80 °C) is not expected to be rapid. An additional dissociative route could involve the hemilabile property of the NiN$_2$S$_2$ ligand, as has been established for NiN$_2$S$_2$W(CO)$_4$ complexes.[12] These mechanisms are expressed in Figure 6, as dissociative paths A and B. A more attractive alternative is the associative path shown in Figure 6, path C, as proposed by van Leeuwen and co-workers,[18] with precedence in work by Natile and co-workers.[28] In addition, five-coordinate intermediates through associated routes have been observed by Brookhart and co-workers when excess CO is added to [(o-MeO-dppe)NiMe(OEt$_2$)]$^+$ to form a methyl dicarbonyl complex, [(o-MeO-dppe)NiMe(CO)$_2$]$^+$, which undergoes insertion to form [(o-MeO-dppe)Ni(C(O)Me)(CO)$_2$]$^+$.[29]

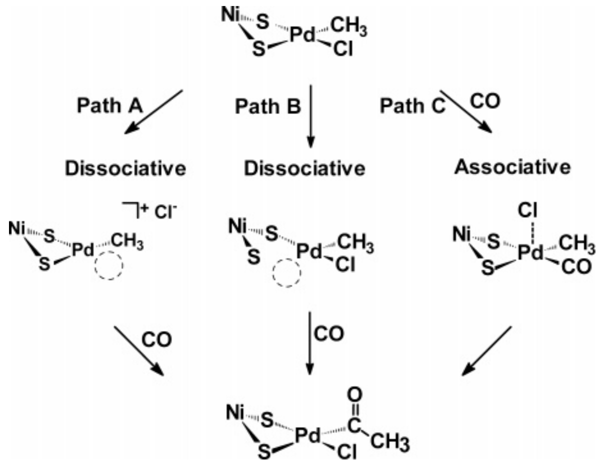

Figure 6. Possible reaction pathways for CO addition/insertion in (**Ni-1**)Pd(CH$_3$)(Cl).

In our studies, some support for the pentacoordinate species comes from infrared studies of CO addition to the (**Ni-1**)Pd(CH$_3$)(Cl) complex in CH$_2$Cl$_2$ held at −80 °C (see the Supporting Information). An infrared spectrum following 5 min of CO purge displayed ν(C=O) bands at 1692 and 1663 cm^{-1}. When the temperature was raised to 22 °C, a terminal ν(C≡O) stretch at 2041 cm^{-1} was observed. This band showed a predictable shift when the solution was purged with ^{13}CO and

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[27] Hill, A. M.; Levason, W.; Webster, M.; Albers, I. *Organometallics* **1997**, *16*, 5641−5647.

[28] (a) Fanizzi, F. P.; Maresca, L.; Natile, G.; Lanfranchi, M.; Tiripicchio, A.; Pacchioni, G. *J. Chem. Soc., Chem. Commun.* **1992**, 333−335. (b) Fanizzi, F. P.; Lanfranchi, M.; Natile, G.; Tiripicchio, A. *Inorg. Chem.* **1994**, *33*, 3331−3339.

[29] Shultz, S. C.; DeSimone, J. M.; Brookhart, M. *J. Am. Chem. Soc.* **2001**, *123*, 9172−9173.

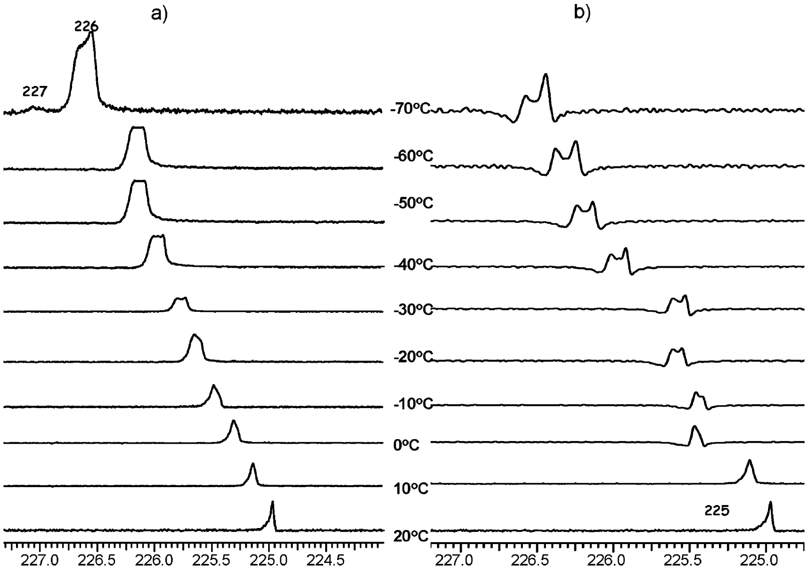

Figure 7. Low-field ^{13}C NMR spectra between −70 and 20 °C of the CO acetyl resonance of (**Ni-1**)Pd(C(O)CH$_3$)(Cl): (a) normal resolution; (b) resolution enhancement by a sine bell function (sb = 0.130 s).

was also shown to disappear when CO gas was removed. Whether the terminal CO band was due to a pentacoordinate palladium species, i.e., (**Ni-1**)Pd(C(O)CH$_3$)(CO)(Cl), or some other carbonyl species, such as the four-coordinate (η^1-NiN$_2$S$_2$-Pd(C(O)CH$_3$)(CO)(Cl)) cannot be determined. It should be noted that the ^{13}C NMR spectrum of the isotopically labeled product did not show resonances in the 190 ppm region that would suggest Pd^0 or Ni^0 as tetracarbonyls. Hence, at this point no conclusion about the identity of the product with the ν(C≡O) stretch at 2041 cm^{-1} can be made.

Temperature-Dependent ^{13}C NMR Spectra of (Ni-1)Pd(C(O)CH$_3$)(Cl). The ^{13}C NMR spectrum at −80 °C of the (**Ni-1**)Pd(C(O)CH$_3$)(Cl) complex shows two resonances in the acetyl region, a major one at 226 ppm and a smaller one at 227 ppm. As seen in Figure 7a, warming the sample in 10 °C increments led to both broadening and a shift of the signal, ultimately yielding one signal at 225 ppm. Figure 7b also displays a resolution enhancement of the signals (produced from a sine bell function),[30] which shows that the distinctiveness of the two resonances disappeared at ca. 0 °C. It should be noted that when the sample is cooled back to −30 °C, both carbonyl signals reappear, indicating reversibility.

Assuming that the temperature dependence of the acetyl resonance reflects signals from a single molecule and intramolecular rearrangements, its interpretation may benefit from examination of the solid-state structure of (**Ni-1**)Pd(CH$_3$)(Cl) and the known molecular structures of several acetylpalladium complexes.[16,18] The latter show that the acetyl (C=O) ligand is oriented perpendicular to the PdL$_2$C$_2$ plane square plane, as shown in the structure of the [(o-phen)Pd(C(O)CH$_3$)(CO)]$^+$ complex (Figure 8). Superimposed on this structure is that of (**Ni-1**)Pd(CH$_3$)(Cl). If one assumes that the orientation of the acetyl (C=O) group is similar to that of the (o-phen)Pd derivative, two isomeric forms of the (**Ni-1**)Pd(C(O)CH)$_3$(Cl) are possible. The “up” positions the C=O group in close contact with the NiN$_2$S$_2$ ligand. Alternatively, the C=O group may be oriented downward from the NiN$_2$S$_2$ ligand (Figure 9). Assuming these structural forms have a significant lifetime in solution, then the VT NMR results could reflect the interconversion between isomers, represented by the stick drawings in Figure 9.

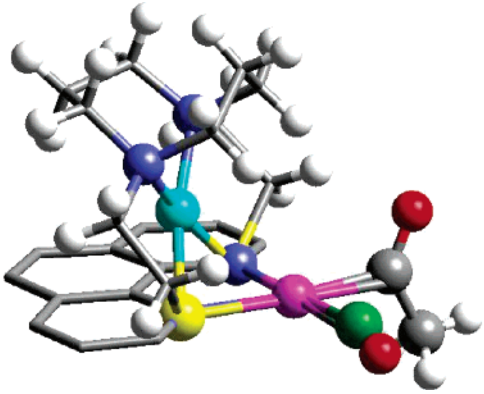

Figure 8. Ball-and-stick representation of an overlay of the molecular structures of (**Ni-1**)Pd(CH$_3$)(Cl) and [(o-phen)Pd(C(O)-CH$_3$)(CO)]$^+$, illustrating the orientation of the acetyl (C=O) group perpendicular to PdS$_2$CCl and parallel to the **Ni-1** ligand. Hydrogen atoms were added on the **Ni-1** ligand and the CH$_3$ group of the acetyl to illustrate the steric influence of the **Ni-1** ligand.

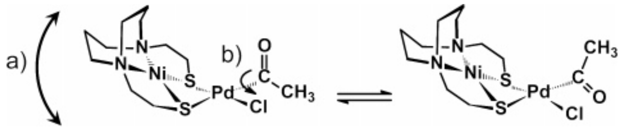

Figure 9. Stick drawings illustrating isomerization involving either (a) buckling of the NiN$_2$S$_2$ ligand and Pd(C(O)CH$_3$(Cl) unit at the sulfur hinges or (b) acetyl carbonyl bond rotation.

While the mechanism of this site exchange is unknown, equilibration could occur via a buckling of the NiN$_2$S$_2$ ligand with respect to the palladium square plane (Figure 9), a process which has precedence in a VT NMR study of the [**Ni-1***]-W(CO)$_4$ complex.[10] Alternatively, a rotation around the Pd−(C(O)Me) bond could also result in the equilibration (Figure 9).

^{13}C NMR Study of CO and Ethylene Uptake by [(Ni-1)-Pd(CH$_3$)(OEt$_2$)][BAr′$_4$]. As background for the CO/olefin

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[30] Mann, B. E.; Akitt, J. W. In *NMR and Chemistry*, 4th ed.; Thornes, N., Ed. CRC Press: Boca Raton, FL, 2000; pp 161−162.

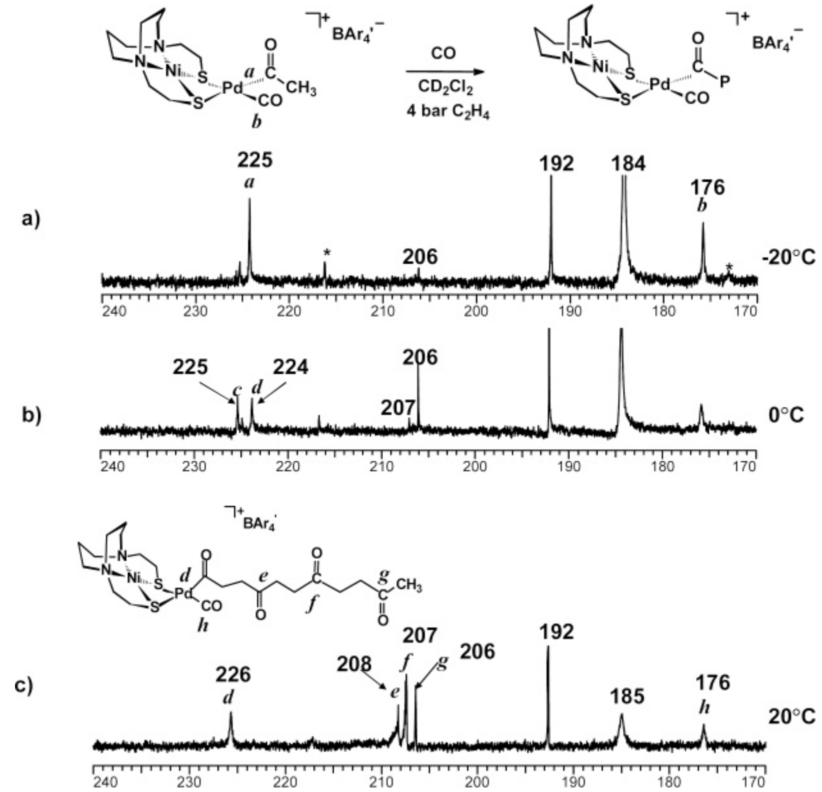
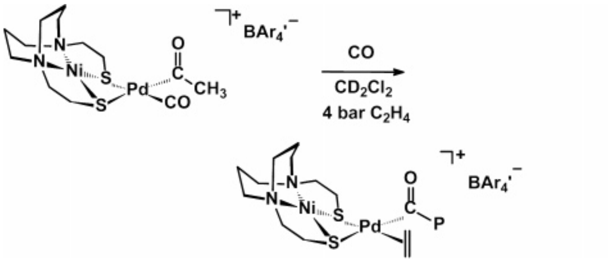


Figure 10. ^{13}C NMR spectral monitoring of the reaction of ethylene and CO with $[(\mathbf{Ni\text{-}1})Pd(C(O)CH_3)CO)]^+$ in CD_2Cl_2: (a) −20 °C; (b) 0 °C; (c) 20 °C.

copolymerization studies, the reaction progress of ^{13}CO and ethylene gas uptake by $[(\mathbf{Ni\text{-}1})Pd(CH_3)(OEt_2)]^+$ was monitored by ^{13}C NMR spectroscopy. A 21 mM sample of $[(\mathbf{Ni\text{-}1})Pd(CH_3)(OEt_2)]^+$ in CD_2Cl_2 was pressurized with 8 bar of ^{13}C-labeled CO gas at −80 °C, and the ^{13}C NMR spectrum was recorded within a 5 min period, with results as described in eq 5. Two resonances characteristic of the acetyl carbonyl complex $[(\mathbf{Ni\text{-}1})Pd(C(O)CH_3)(CO)]^+$ appeared at 225 ppm (the acetyl C═O carbon) and 176 ppm (the CO). In addition, resonances for the free ^{13}CO and for the $Ni(CO)_4$ impurity were evident.

While it was maintained at −80 °C, the sample was depressurized to 1 bar followed by addition of ethylene to a total pressure of 5 bar (eq 7). The ^{13}C NMR spectrum was recorded at −80 °C and at temperature increases of 10 °C increments. When the sample was warmed, minor spectral changes were observed. Two resonances are seen in the acetyl C═O carbon region, at 224 and 225 ppm. Brookhart and coworkers have shown that the acetyl C═O carbon resonance of $[(o\text{-}phen)Pd(C(O)CH_3)(\eta^2\text{-}CH_2{=}CH_2)]^+$, 217 ppm, is positioned ca. 6 ppm upfield relative to the carbon acetyl resonance of $[(o\text{-}phen)Pd(C(O)CH_3)(CO)]^+$ (223 ppm).[16] The changes observed in our study are too minor to argue for a $[(\mathbf{Ni\text{-}1})Pd(C_c(O)CH_3)(\eta^2\text{-}CH_2{=}CH_2)]^+$ intermediate and are more likely due to differences in insertion products, $[(\mathbf{Ni\text{-}1})Pd(C_c(O)R_{poly})(CO)]^+$.



(7)

At 20 °C resonances are observed at 208, 207, and 206 ppm and are assigned to the carbon signals from ketone-like end groups after three consecutive CO/ethylene insertions in $[(\mathbf{Ni\text{-}1})Pd(C(O)CH_3)CO)]^+$, forming a growing polymer chain (Figure 10c). This is consistent with a decrease in the concentration of free ^{13}CO in solution: i.e., the resonance at 184 ppm. No change was observed in the intensity of the resonance at 192 ppm assigned to $Ni(CO)_4$.

Since no spectral changes were observed at temperatures lower than −20 °C, it can be concluded that ethylene does not easily replace CO. The appearance of new signals at $T > -20$ °C suggests that a CO/$CH_2{=}CH_2$ exchange has occurred, along with some ethylene insertion. As may be implied from Figure 2, ethylene displacement of CO in the resting state of the catalyst $[(o\text{-}phen)Pd(C(O)CH_3)(CO)]^+$, to form the ethylene acetyl complex $[(o\text{-}phen)Pd(C(O)Me)(\eta^2\text{-}CH_2CH_2)]^+$, is thermodynamically uphill.[16] Therefore, it is reasonable that a metal center with a very electron rich ligand will prefer to have a good π-acceptor ligand such as CO rather than ethylene, as evidenced by the presence of a Pd-bound terminal CO-trapped species during the reaction. Hence, the resting state of the catalyst with a metallodithiolate ligand is the species $[(\mathbf{Ni\text{-}1})Pd(C(O)CH_3)(CO)]^+$ (Figure 11a) and, due to the high binding affinity of CO for the Pd^{2+} metal center, ethylene insertion is slow. The absence of resonances in the 240 ppm region (Figure 10) indicate the five-membered β-chelate (Figure 11c) and six-membered γ-chelate intermediates (Figure 11d) are not prevalent in the CO/C_2H_4 reaction. This result is in contrast to what was noted under mild reaction conditions with the diphosphine Pd metal based systems.[17]

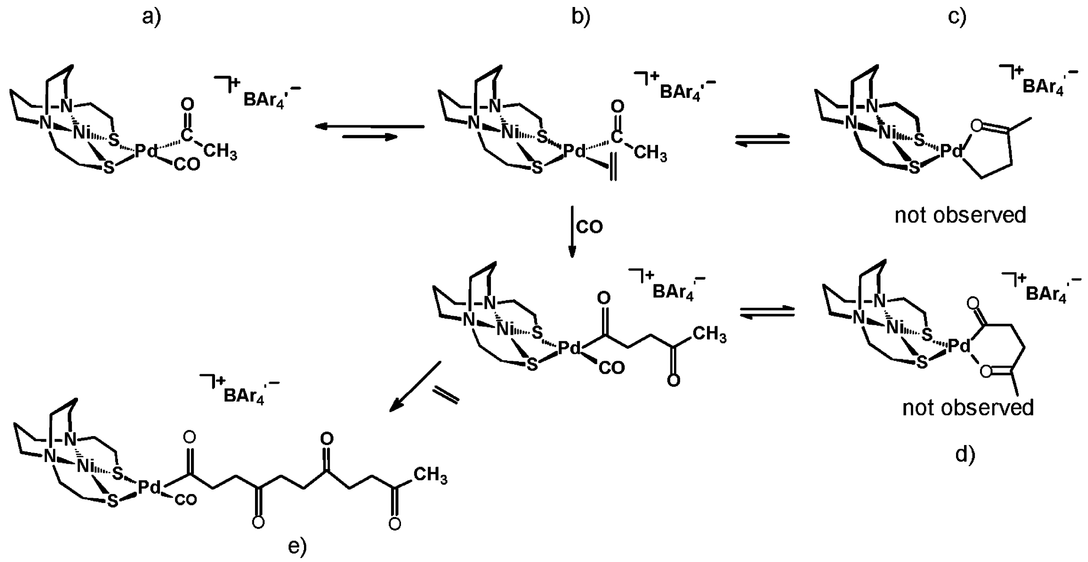
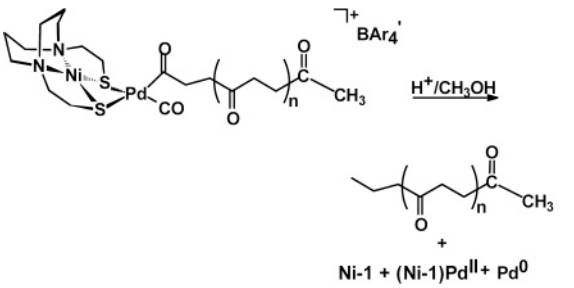


Figure 11. Proposed mechanistic cycle for the CO/C_2H_4 coupling reaction.

CO/Ethylene Copolymerization with [(Ni-1)Pd(CH_3)(OEt_2)][BAr′$_4$]. Having shown that CO and ethylene insertion can occur with [(**Ni-1**)Pd(CH_3)(OEt_2)]$^+$, bulk copolymerization studies were conducted. The catalytic species was formed in a CH_2Cl_2 solution by reacting the (**Ni-1**)Pd(CH_3)$_2$ and HBAr′$_4$ precursors in predried glassware prior to transfer into the stainless steel high-pressure Parr autoclave. Pressurization with CO was followed by ethylene. Over the course of 24 h at room temperature, a light gray to white product, characteristic of polyketone, precipitated from the reaction mixture. Polyketones are known to be soluble in cresol and (the highly toxic) hexafluoro-2-propanol, permitting analysis by NMR, IR, and mass spectroscopy. The solution infrared spectrum of the polymer in $(CF_3)_2CHOH$ has a distinctive ν(C═O) stretch at 1704 cm^{-1} in the C═O region (the KBr pellet has ν(C═O) 1692 cm^{-1}). The room-temperature ^{13}C NMR spectrum of the copolymer displays two resonances at 220 and 43 ppm, corresponding to the C═O moiety and CH_2 groups from ethylene insertion, respectively (see the Supporting Information). These assignments correspond to those reported in the literature.[13,31]

A red residue found in the opened autoclave was collected after several polymer runs. Mass spectral analysis indicated it to be the red trimetallic species, [(**Ni-1**)$_2$Pd]$^{2+}$. As shown in eq 8, its presence derives from chain termination with acid release of the polymer, which also produces [(**Ni-1**)Pd^{2+}], presumably as a solvate. In such a case redistribution to form the stable trimetallic species [(**Ni-1**)$_2$Pd]$^{2+}$ is reasonable.



(8)

End group analysis of the polymer according to the ^{1}H NMR spectrum shows a small resonance of the CH_3 group from the ketonic end group at 2.17 ppm, slightly upfield from the resonance of the CH_2 groups at 2.73 ppm, consistent with literature reports.[32] The MALDI-TOF mass spectral analysis of the copolymer also confirmed that one of the end groups is a ketone (see the Supporting Information). The polymer was characterized by the presence of the cationic (adducts of potassium ion) oligomers, which differ from each other by the mass of one repeat unit (*m*/*z* 56). On the basis of the integration of the ketonic CH_3 group relative to the $-CH_2CH_2$ repeat unit, the average molecular mass of the polymer was computed to be approximately 3700 g/mol, corresponding to ca. 65 repeat units.

Table 1. Effect of [CO] and [Ethylene] on Productivity[a]

run	CO pressure (psi)	$CH_2{=}CH_2$ pressure (psi)	yield (g)	g of PK/ g of Pd[b]	productivity[c]
1	100	100	0.1	9.4	0.4
2	100	200	0.3	45.8	1.9
3	100	300	0.4	60.0	2.5

[a] PK = polyketone. Conditions: volume of solvent, 25 mL of CH_2Cl_2; [catalyst] = 0.056 mmol; temperature, 30 °C; run time, 24 h. [b] g of polyketone/g of Pd. [c] Productivity = g of polyketone/((g of Pd) h).

Effect of Monomer Concentration and Solvent on Polyketone Productivity with [(Ni-1)Pd(CH_3)(OEt_2)][BAr′$_4$]. To examine the effect of monomer concentration or solvent type on polyketone formation, the following experiments were carried out. Approximately 50−75 mg (0.037−0.056 mmol) of [(**Ni-1**)Pd(CH_3)(OEt_2)]$^+$ catalyst in 25 mL of solvent was added to the stainless steel high pressure autoclave held at 30 °C with varying ethylene monomer concentration while the CO pressure was kept constant over a 24 h period. Solvent dependence was also explored.

The data in Table 1 illustrate that an increase in ethylene monomer concentration increases the polymer yield. These results are consistent with those of Brookhart and co-workers, in that a greater concentration of ethylene is required to shift the reaction equilibrium toward the ethylene-bound side.[22] Copolymerization reactions conducted in more donating solvents such as CH_3CN and THF showed lower production than in CH_2Cl_2 (Table 2), suggesting that better coordinating solvents

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[31] Zhao, A. X.; Chien, J. C. W. *J. Polym. Sci., Polym. Chem.* **1992**, *30*, 2735.

[32] Wu, T. K.; Ovenall, D. W.; Hoen, H. H. In *Applications of Polymer Spectroscopy*, 1st ed.; Brame, E. G., Ed.; Academic Press: New York, 1978; p 19.

Table 2. Effect of Solvent on Productivity[a]

solvent	time (h)	yield of PK (g)	g of PK/g of Pd[b]	productivity[c]
CH_2Cl_2	24	0.056	14.1	0.6
CH_3CN	24	0.035	8.9	0.4
THF	24	0.031	7.8	0.3

[a] PK = polyketone. Conditions: volume of solvent, 25 mL; [catalyst] = 0.037 mmol; temperature, 30 °C; run time, 24 h; $CO/CH_2{=}CH_2$ (100 psi/200 psi). [b] g of polyketone/g of Pd. [c] Productivity = g of polyketone/((g of Pd) h).

compete with ethylene and CO for the open site, again consistent with the studies of Brookhart and co-workers on the (diimine)-Pd^{2+} system.[16] Other non-coordinating solvents, while ideal for the above reasons, are not practical for copolymerization with our approach, because of low catalyst solubility. Interestingly, regardless of the solvent the ^{13}C NMR analysis showed that the copolymer remains alternating.

In comparison to a current diphosphine-based industrial catalyst, (diMe-Si-AXPHS)Pd^{2+} (diMe-Si-AXPHS = di-*o*-anisylphosphinodimethylsilane), which produces a TOF of 40 000 g of polyketone with 50 bar of CO/ethylene at 90 °C in methanol,[33] the $[(\textbf{Ni-1})Pd(CH_3)(OEt_2)]^+$ catalyst was much less efficient, producing a TOF of 2.5 g at 30 °C under 7 bar of CO/ethylene. The low productivity is likely due to the very stable resting state complex $[(\textbf{Ni-1})Pd(C(O)CH_3)(CO)][BAr'_4]$.

Summary

The salient features of the nickel dithiolate ligand palladium derivatives as CO/olefin copolymerization catalysts are as follows.

(1) $[(\textbf{Ni-1})Pd(CH_3)(OEt_2)]^+$ is readily generated from $(\textbf{Ni-1})Pd(CH_3)_2$ by addition of $HBAr'_4$, demonstrating the reactivity of the $Pd(CH_3)_2$ precursor and the stability of the **Ni-1** ligand−palladium interaction in the presence of acid.

(2) CO addition to the $[(\textbf{Ni-1})Pd(CH_3)(OEt_2)]^+$ cation results in CO uptake, CO/CH_3 migratory insertion, and the production of $[(\textbf{Ni-1})Pd(C(O)CH_3)(CO)]^+$ at the time of mixing at −80 °C. A similar rate of CO uptake is observed for $(\textbf{Ni-1})Pd(CH_3)(Cl)$, with the product being $(\textbf{Ni-1})Pd(C(O)CH_3)(Cl)$. In comparison to traditional neutral $(L_2)Pd(CH_3)(X)$ and cationic metal complexes $[(L_2)Pd(CH_3)]^+(X)^-$ the CO uptake and insertion reaction is faster in the $(\textbf{Ni-1})Pd^{II}$ metal complexes.

(3) Low-pressure NMR studies of CO/ethylene (ca. 5 bar) addition to $[(\textbf{Ni-1})Pd(CH_3)(OEt_2)]^+$ demonstrate fundamental steps in the catalysis of alternating polyketone.

(4) The results of in situ NMR spectral studies as well as bulk copolymerization studies can be interpreted in terms of the now classic mechanism proposed for the $[(L_2)Pd(CH_3)(OEt_2)]^+$ (L = diimine) catalysts.[16]

The palladium-based reaction chemistry observed in this study is readily ascribed to the presence of an L_2 ligand with better electron donating ability than the traditional diphosphine and diimine ligands. This conclusion is consistent with the previously established relative donor ability of NiN_2S_2, diimines, and diphosphines toward $W(CO)_4$. This conclusion is also reasonable, as CO will have a greater binding affinity for palladium in the presence of better electron donating ligands. Ancillary to this is the lack of keto chelate structures in the $(NiN_2S_2)Pd$/CO/olefin products. The low productivities in CO/olefin copolymerization observed in the $(NiN_2S_2)Pd$ system suggest that, as supporting ligands in catalysis, nickel dithiolates would be better suited to reaction chemistry involving oxidation state increases at the attached metal. We also note that reactions involving sulfur-bridged bimetallics may serve as homogeneous analogues to sulfided surface catalysts.

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Supporting Information Available: Additional UV−vis, infrared, MALDI-TOF, and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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