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Palladium Methoxide and Carbomethoxy Complexes: Synthesis and Molecular Structure of (bipy)Pd(CO_2CH_3)$_2$

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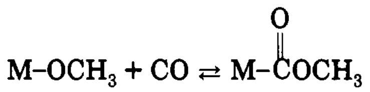
Summary: Bis(carbomethoxy)palladium bipyridine is synthesized by the reaction of (bipy)PdCl$_2$ with LiOCH$_3$ under a CO atmosphere. NMR evidence for the apparent precursor to (bipy)Pd(CO$_2$CH$_3$)$_2$, i.e. (bipy)Pd(OCH$_3$)$_2$, was obtained in situ by NMR spectroscopy. (bipy)Pd(CO$_2$CH$_3$)$_2$ crystallizes in the monoclinic space group C2/c with a = 16.851 (10) Å, b = 12.137 (5) Å, c = 7.088 (4) Å, β = 97.99 (5)°, V = 1435 (1) Å^3, and Z = 4. The final refinement indices are R = 0.0681 and R(w) = 0.0774. The compound is thermally stable in methanol at temperatures up to 60 °C; it decomposes in THF to yield methanol, bipyridine, and palladium metal.

Carbomethoxy compounds of transition metals, i.e. compounds that contain the M–CO_2CH_3 group, have been prepared by several routes including the nucleophilic attack of methoxide on coordinated carbon monoxide, oxidative addition of haloformates, and CO insertion into an M–OCH_3 bond.[1–3] The latter route represents one of the fundamental steps in the oxidative carbonylation of methanol to yield either dimethyl carbonate or dimethyl oxalate.[4–6]



$$\mathrm{M{-}OCH_3 + CO \rightleftharpoons M{-}\overset{\displaystyle O}{\overset{\|}{C}}OCH_3}$$

Carbonyl insertion into a M–OCH_3 band has been demonstrated in (dppe)Pt(OCH_3)CH_3, which reacts with CO at room temperature to yield (dppe)Pt(CO_2CH_3)(CH_3).[7] Formation of the iridium carbomethoxy complex, Ir(PPh_3)$_2$(CO_2CH_3)(CO)$_2$, from the methoxide complex, Ir(PPh_3(CO)(OCH_3)), occurs via the ionic intermediate, $[Ir(PPh_3)_2(CO)_3]^+[OCH_3]^-$, with nucleophilic attack on coordinated CO by methoxide.[8]

Although palladium catalysts can be used to effect the carbonylation of methanol to yield carbonates and oxalates, relatively few examples exist of stable palladium compounds that model potential reaction intermediates.[2,9,10] In particular palladium methoxide compounds are not well characterized and only a few palladium carbomethoxy compounds have been prepared; these include Pd(PPh_3)$_2$(CO_2CH_3)Cl,[2] Pd(PPh_3)$_2$(CO_2CH_3)$_2$,[7] and Pd(PPh_3)$_2$(CO_2CH_3)(OAc).[10] Here we describe the synthesis and molecular structure of (bipy)Pd(CO_2CH_3)$_2$ (bipy = 2,2′-bipyridine), the first carbomethoxy compound of palladium to be structurally characterized. The corresponding methoxide, (bipy)Pd(OCH_3)$_2$, is characterized in situ by NMR spectroscopy and by its reaction with CO.

Simple platinum methoxide complexes, such as *trans*-Pt(PMe_3)$_2$(R)(OCH_3), may be prepared by the metathesis of $NaOCH_3$ with *trans*-Pt(PMe_3)$_2$(R)Cl.[11] The bis(methoxy) compound (dppe)Pt(OCH_3)$_2$ is prepared similarly from (dppe)$PtCl_2$, and the cis alkyl methoxides (dppe)Pt(R)(OCH_3) are prepared from (dppe)Pt(R)Cl.[12] The platinum methoxides are thermally unstable; (dppe)Pt(OCH_3)$_2$ decomposes at 25 °C to yield methanol, formaldehyde, and CO.[12]

A stable palladium alkyl methoxide complex can be prepared when the alkyl group is electron withdrawing. Thus, *trans*-(C_6F_5)Pd(PPh_3)$_2$(OCH_3) has been isolated.[13] The only palladium alkoxide complexes to be structurally characterized are the phenoxides. For example, phenol adds to Pd(PPh_3)$_2$ to yield *trans*-HPd(PPh_3)$_2$(OPh)·HOPh, which has been characterized by X-ray crystallography.[12] An alkylpalladium phenoxide can also be prepared from the reaction of (dmpe)$PdMe_2$ and phenol to yield (dmpe)Pd(CH_3)(OPh).[15]

Experimental Section

All reactions and manipulations were performed under nitrogen or argon by standard Schlenk and glovebox techniques. Palladium salts were obtained from Aesar; lithium methoxide and 2,2′-bipyridine were obtained from Aldrich. Solvents were distilled under nitrogen from an appropriate drying agent, e.g. CH_2Cl_2 from P_2O_5 and CH_3OH from Mg(OCH_3)$_2$ prepared in situ from Mg turnings. The palladium compound, (bipy)$PdCl_2$,[16] was prepared by literature methods. NMR spectra were recorded either on a Bruker WP200 or a Varian RU400 NMR spectrometer.

(bipy)Pd(CO_2CH_3)$_2$. A 100-mL round-bottom flask was charged with 0.73 g (2.8 mmol) of (bipy)$PdCl_2$ and 0.32 g (8.4 mmol) of $LiOCH_3$ under CO. After being cooled to to −78 °C, solvent, 25 mL of CH_2Cl_2 and 25 mL of methanol, was added.

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Table I. Crystal Data for (bipy)Pd(CO_2CH_3)$_2$

$C_{12}H_{14}N_2O_4Pd$	fw = 356.66
a = 16.851 (10) Å	space group $C2/c$
b = 12.137 (5) Å	T = 298 K
c = 7.088 (4) Å	λ = 0.710 73 Å
β = 97.99 (5)°	ρ_{calc} = 1.761 mg cm^{-3}
V = 1435 Å^3	μ(Mo Kα) = 1.290 mm^{-1}
Z = 4	transm = 0.3866–0.7077
R = 0.0681	empirical abs corr
R(w) = 0.0744	

The reaction mixture was allowed to stir while warming to room temperature. Between 0 and 20 °C the solids dissolved to give a yellow solution. After 3 h a black precipitate began to form. At this time the solution was filtered and the solvent removed. The solids were extracted with CH_2Cl_2 (3 × 20 mL) at room temperature. The combined extracts were concentrated and cooled to −78 °C to yield a yellow crystalline solid, 0.55 g (62%).

(bipy)Pd(OCH_3)$_2$. Attempts to isolate the bis(methoxy) compound (bipy)Pd(OCH_3)$_2$ gave only starting material (bipy)$PdCl_2$. Evidence for its formation was obtained as follows. In a typical NMR reaction (bipy)$PdCl_2$ was slurried in 0.5 mL of CH_2Cl_2/CH_3OH (1/1, v/v). The bipyridyl resonances were observed at 9.40 (d), 8.15 (t), 0.05 (d), and 7.60 (t) ppm. Addition of solid $LiOCH_3$ is aliquots caused the (bipy)$PdCl_2$ to dissolved. At stoichiometries $LiOCH_3/Pd < 2$ as many as 10 multiplets are observed in the bipyridyl region. When the ratio is ≥3 resonances are observed at 8.50 (d), 8.09 (d), 8.03 (t), and 7.55 (t) ppm.

Removal of the solvent or precipitation with pentane yields a solid which when extracted with CH_2Cl_2 yields only (bipy)$PdCl_2$.

Analytical Data for (bipy)Pd(CO_2Me)$_2$. Anal. Calcd for $C_{12}H_{14}N_2O_4Pd$: C, 44.2; H, 3.71; N, 7.36. Found: C, 42.6; H, 3.69; N, 6.97. ^1H NMR ($CDCl_3$): 8.71 (2, d), 8.16 (2, d), 8.07 (2, t), 7.42 (2, t), 3.73 (3, s) ppm. ^{13}C NMR ($CDCl_3$): 187.3, 153.5, 151.1, 138.7, 125.6, 121.5, 49.6 ppm. IR (Nujol): ν(CO) 1633 cm^{-1}.

Crystals of (bipy)Pd(CO_2Me)$_2$ were grown by the slow diffusion of hexane into a CH_2Cl_2 solution at room temperature. A small crystal of dimensions 0.15 × 0.15 × 0.20 mm was mounted in a sealed capillary for the X-ray structure determination. Indexing and data collection were performed on a Nicolet R3m/v diffractometer with Mo Kα radiation at 298 °C. The unit cell based on the least-squares fit of 25 reflections with $15° < 2\theta < 30°$ was monoclinic $C2/c$, with a = 16.851 (10) Å, b = 12.137 (15) Å, c = 7.088 (4) Å, β = 97.99 (5)°, V = 1435 (11) Å^3, and Z = 4.

Data were collected by the θ–2θ scan technique in the range 3.5–55°. The scan rate varied with peak intensity, 10.1-19.5°/min. Three standard reflections were measured after every 200 reflections and showed no loss in intensity during data acquisition. A total of 3578 reflections were collected of which 1663 were independent (R_{int} = 2.25%). Of the independent reflections 1383 had $F > 3\sigma(F)$; these reflections were used to determine the structure. The crystal and refinement parameters are summarized in Table I; a more complete table is available with the supplementary material.

All calculations were performed on a micro VAX II with the SHELXTL PLUS crystallographic package provied by Nicolet. Neutral-atom scattering factors were obtained from the standard source, and the effects of anomalous dispersion were included in F_c.[17] The structure was solved by direct methods. Refinement was accomplished by full-matrix least squares to minimize the function $\Sigma w(F_o - F_c)^2$. Unit weights were used. The final residuals were R_1 = 0.0681 and R_2 = 0.0774. Atomic coordinates are compiled in Table II. Atomic displacement parameters are available as supplementary material. Selected bond distances and angles are given in Table III.

Results and Discussion

The reaction of (bipy)$PdCl_2$ with excess $LiOCH_3$ in methanol/CH_2Cl_2 at 25 °C yields a bright yellow solution. The ^1H NMR spectrum of the yellow solution shows a set of 2,2′-bipyridine signals consistent with the formation of (bipy)Pd(OCH_3)$_2$. Assignment of signals arising from coordinated methoxide was not possible due to the presence of methanol solvent. Attempts to isolate (bipy)Pd(OCH_3)$_2$ were unsuccessful. For example, removal of the solvent yielded a solid that could not be extracted in high concentration into THF, methylene chloride, or methanol. Traces apparently dissolve in CH_2Cl_2; the NMR spectrum in this case however revealed the presence of only starting material, i.e. (bipy)$PdCl_2$.

Table II. Atomic Coordinates (×10^4)

	x	y	z
Pd(1)	0	6725 (1)	2500
N(1)	747 (4)	5365 (5)	2107 (8)
C(1)	1512 (4)	5419 (7)	1756 (12)
C(2)	1960 (4)	4487 (8)	1588 (13)
C(3)	1631 (5)	3479 (7)	1708 (13)
C(4)	844 (5)	3407 (7)	2063 (12)
C(5)	425 (3)	4359 (6)	2271 (10)
C(6)	748 (5)	7914 (7)	1956 (14)
C(7)	1012 (9)	9292 (11)	−235 (21)
O(1)	1399 (5)	8091 (7)	2799 (15)
O(2)	461 (4)	8525 (6)	395 (11)

Table III. Selected Bond Distances (Å) and Angles (deg)

	Distances		
Pd(1)–C(6)	1.989 (9)	C(6)–O(1)	1.192 (11)
Pd(1)–N(1)	2.118 (6)	C(6)–O(2)	1.363 (11)
	Angles		
C(6)–Pd(1)–C(6a)	87.0 (5)	Pd(1)–C(6)–O(1)	126.6 (8)
C(6)–Pd(1)–N(1)	97.8 (3)	Pd(1)–C(6)–O(2)	112.9 (6)
N(1)–Pd(1)–N(1a)	77.6 (3)	O(1)–C(6)–O(2)	120.4 (9)
N(1)–Pd(1)–C(6a)	174.5 (3)		

When pressurized with CO (1–2 atm), the yellow solutions darken and a small quantity of black precipitate forms. NMR analysis of the reaction mixture shows the formation of bipyridine resonances that correspond to (bipy)Pd(CO_2CH_3)$_2$. Also seen are an intermediate set of bipyridine resonances that are consistent with formation of an unsymmetrical bipyridine ligand. This could occur by the stepwise insertion of CO into the palladium–methoxide bond. Continued standing gives a copious black precipitate; analysis of the remaining solution by GC–mass spectroscopy shows the presence of bipyridine. Workup of the reaction with CO after several hours was accomplished by removal of the solvent and recrystallization from CH_2Cl_2/hexane. The product, (bipy)Pd(CO_2CH_3)$_2$, is obtained as a yellow crystalline solid.

The molecular structure of (bipy)Pd(CO_2CH_3)$_2$, as determined by X-ray crystallography, is shown in Figure 1. The molecule is square planar as expected and lies on a 2-fold rotation axis in the crystal. The CO_2CH_3 groups are planar and bisect the Pd(1), N(1), C(6), N(1a), C(6a) plane at an angle of 67°. The methoxy groups are staggered above and below the plane and are related by the crystallographic 2-fold rotation axis. The C(6)–O(2) and Pd(1)–C(6) bond lengths are typical for single bonds, and the C(6)–O(1) bond is representative of carbon–oxygen double bonds. The geometry and the normal bond lengths suggest that there is little π bonding between the palladium and the carbomethoxy group.

Several carboalkoxy complexes of group 8–10 metals have been structurally characterized. For example, in (C_5Me_5)Rh(CO)(CO_2Et)$_2$, prepared from the carbonylation of [(C_5Me_5)$RhCl_2$]$_2$ in ethanol in the presence of NEt_3,

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[17] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

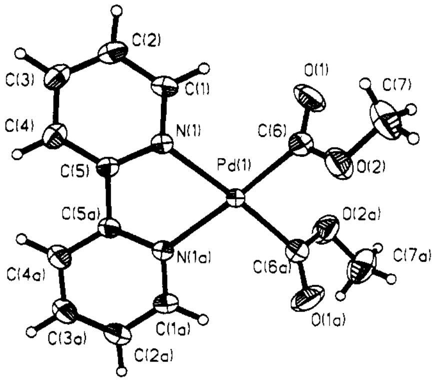

Figure 1. ORTEP representation of 1 showing 40% probability thermal ellipsoids.

the carboethoxy ligands are in adjacent positions.[18] Reductive elimination yields diethyl oxalate.

The bis(carboethoxy) complex of platinum, $Pt(PPh_3)_2(CO_2Et)_2$, is isolated as the trans isomer.[19] The planar $-CO_2-$ groups are oriented perpendicular to the coordination plane about platinum. An iridium carbomethoxy complex, $Ir(I)_2(bipy)(CO)(CO_2Me)$, was prepared by Malatesta et al. by the reaction of CH_3O^- on coordinated carbon monoxide.[19] The X-ray structure of the compound shows that the carbomethoxy group lies in the same plane as the bipyridine ligand in the octahedral complex.[21]

The bis(carbomethoxy) complex prepared here appears to more thermally stable than the previously prepared triphenylphosphine analog, $Pd(PPh_3)_2(CO_2CH_3)_2$, which is reported to thermally decompose in methanol at 50 °C to yield dimethyl oxalate.[7] $(bipy)Pd(CO_2CH_3)_2$ can be recrystallized from methanol at 60 °C without decomposition.

Prolonged heating of $(bipy)Pd(CO_2CH_3)_2$ in methanol at 120 °C in a sealed tube yields a palladium mirror and bipyridine. No other organic products were observed either by NMR or by GC. When a d_8-THF slurry of $(bipy)Pd(CO_2CH_3)_2$ was heated to 60 °C for 2 h, the solids turn black, and NMR spectroscopy reveals that the THF phase contains methanol and bipyridine. Integration shows that bipyridine and methanol are formed in a ratio of ca. 1:2, respectively. No other organic products could be identified by NMR; thus, the source of the proton for the formation of methanol is not clear at this time. It should be noted that only those products soluble in THF are observed; the reaction mixture contains a large quantity of undissolved solids that may have provided the necessary proton for decomposition.

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Supplementary Material Available: Tables of crystal data and data collection details, atomic coordinates and thermal parameters, and bond distances and angles for 1 (5 pages). Ordering information is given on any current masthead page.

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