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Notes

Carbon–Hydrogen Bond Activation of Nitromethane by $[Pd_2Cl_2(\mu\text{-}Me_2PCH_2PMe_2)_2]$: Formation and X-ray Structure of the Face-to-Face Dimer $[Pd_2Cl_2(CH_2NO_2)_2(\mu\text{-}Me_2PCH_2PMe_2)_2]$

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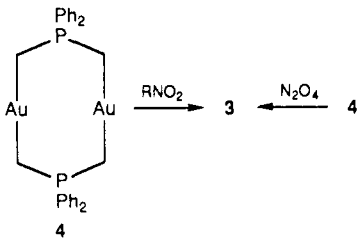
Summary: The complex $[Pd_2Cl_2(\mu\text{-dmpm})_2]$ (dmpm = $Me_2PCH_2PMe_2$) reacts with neat nitromethane at 0 °C to yield $[Pd_2Cl_2(CH_2NO_2)_2(\mu\text{-dmpm})_2]$. The product has been characterized spectroscopically and by X-ray crystallography. Formation of the face-to-face dimer involves carbon–hydrogen bond activation in two nitromethane molecules with concomitant oxidation of two palladium(I) centers to palladium(II). In contrast, the complex $[Pd_2Cl_2(\mu\text{-dppm})_2]$ (dppm = $Ph_2PCH_2PPh_2$) does not react with nitromethane under comparable conditions.

The remarkable reaction chemistry of dinuclear ylide-bridged gold complexes with nitroalkanes and nitroarenes has recently been described by Fackler and co-workers.[1,2] The d^9–d^9 gold(II) dimer, **1**, reacts with nitromethane at 0 °C over a period of several weeks to produce the nitromethylene-bridged complex **2** in a process involving cleavage of *two* C–H bonds in *a single molecule* of nitromethane.[1] In a THF/nitromethane (12:1) mixture at 25 °C, **1** produces the dinuclear nitro compound **3** in a process involving cleavage of the C–N bonds of *two* molecules of nitromethane[2] (Scheme I).

Mechanistic studies[1,2] suggest that **1** is converted to the gold(I) ylide dimer **4**, along with other products, in weakly acidic media. Compound **4** reacts with aliphatic and aromatic nitro compounds, as well as with N_2O_4, to produce **3**. In THF solution, for example, **4** reacts with *p*-nitrotoluene to generate **3**, along with toluene and oligomers derived from THF. Formation of these organic products has been attributed to a radical mechanism for the conversion of **4** to **3**.[2]



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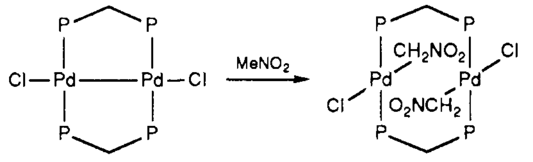
We report here that the d^9–d^9 palladium(I) dimer $[Pd_2Cl_2(\mu\text{-dmpm})_2]^3$ (dmpm = $Me_2PCH_2PMe_2$) (**5**) reacts with nitromethane at or near 0 °C over several weeks to produce not a nitromethylene-bridged complex (c.f. **2**), nor a dinuclear nitro compound (c.f. **3**), but rather the face-to-face (nitromethyl)palladium(II) dimer, $[Pd_2Cl_2(CH_2NO_2)_2(\mu\text{-dmpm})_2]$ (**6**).



5 6

This process thus extends the range of reactions known for d^9–d^9 dimers with nitroalkanes to include not only the cleavage of two C–H bonds in a single molecule (i.e. **1** → **2**) and the cleavage of the C–N bonds of two nitroalkane molecules (i.e. **1** → **3**), but also the cleavage of two C–H bonds in two different nitroalkane molecules (i.e. **5** → **6**).

Results and Discussion

When complex **5** is added to excess, neat nitromethane, an orange solution forms from which light yellow crystals separate after several weeks near 0 °C. The IR spectrum of the isolated material as a KBr pellet shows the presence of nitromethyl ligands by intense absorptions at 1345 and 1491 cm^{-1}, assigned to symmetric and asymmetric stretching modes of the nitro group. A single-crystal X-ray structure determination (Figure 1) revealed that this product is the face-to-face (nitromethyl)palladium(II) dimer, **6**. Table I shows crystal and X-ray diffraction data, Table II shows positional parameters and thermal parameters, and Table III shows selected bond lengths and angles. The structure shows that the two palladium centers (separated by 3.3125 Å) are approximately square planar with the nitromethyl groups mutually trans about the palladium–palladium axis. The geometry of the nitromethyl ligand resembles that found in *trans*-bis(dimethylglyoximato)(nitromethyl)(pyridine)cobalt(III), the only metal–nitromethyl complex previously characterized by X-ray crystallography of which we are aware.[4]

Attempts to follow the solution chemistry involved in the transformation of **5** to **6** have largely been frustrated by the slow rate of conversion (several weeks near 0 °C) and the precipitation of **6**, which is largely insoluble in common organic solvents, from solution as it is formed.

Several pathways can be envisaged for the conversion of **5** to **6**, including routes where molecular hydrogen is

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[1] Knachel, H. C.; Dudis, D. S.; Fackler, J. P., Jr. *Organometallics* **1984**, *3*, 1312.

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[3] (a) Kullberg, M. L.; Kubiak, C. P. *Organometallics* **1984**, *3*, 632. (b) Kullberg, M. L.; Lemke, F. R.; Powell, D. R.; Kubiak, C. P. *Inorg. Chem.* **1985**, *24*, 3589.

[4] Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *Inorg. Chem.* **1981**, *20*, 2722.

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Scheme I

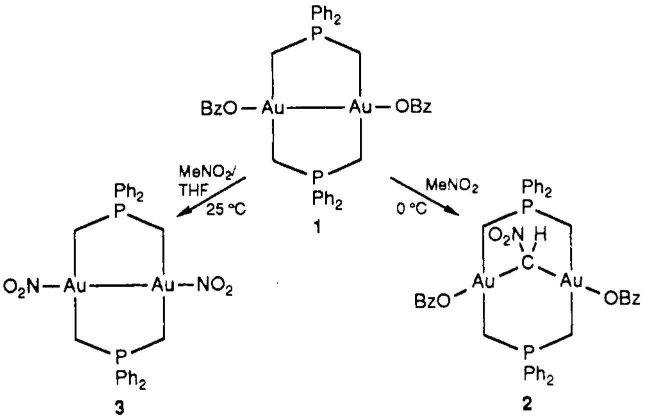

Table I. Crystal Data and Experimental Data

formula	$C_{12}H_{32}Cl_2Pd_2N_2O_4P_4$
cryst color	yellow
cryst habit	needles
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	7.481 (2)
b, Å	14.665 (2)
c, Å	11.132 (1)
β, deg	100.24 (1)
V, Å^3	1201.8
Z	2
D(calcd), g cm^{-3}	1.868
cryst dimens, mm	0.22 × 0.06 × 0.04
temp, °C	21 ± 1
μ (Mo Kα), cm^{-1}	14.36
λ, Å	0.71073
scan mode	ω–2θ
ω scan width, deg	0.8 + 0.344 tan θ
2θ range, deg	4–52
no. of collcd data	2650
no. of unique data	2461
no. of unique data with $F_o^2 > 3.0\sigma(F_o^2)$	1734
range in h	0–9
range in k	0–18
range in l	−13 to +13
no. of variables	118
final residual, e Å^{-3}	0.49
R	0.032
R_w	0.039

Table II. Positional Parameters and Thermal Parameters for 6[a]

atom	x	y	z	B, Å^2
Pd1	0.05873 (5)	0.40318 (2)	0.07304 (3)	2.134 (6)
Cl1	−0.2223 (2)	0.4482 (1)	0.1234 (1)	4.06 (3)
P1	0.2161 (2)	0.48447 (9)	0.2372 (1)	2.40 (2)
P2	−0.1035 (2)	0.33274 (9)	−0.0978 (1)	3.21 (3)
O1	0.4204 (7)	0.2515 (3)	0.1874 (5)	7.5 (1)
O2	0.2529 (8)	0.1955 (3)	0.0324 (5)	7.0 (1)
N1	0.3289 (7)	0.2605 (4)	0.0868 (5)	4.5 (1)
C1	0.2998 (7)	0.3519 (4)	0.0351 (5)	3.5 (1)
C2	0.2816 (8)	0.5942 (4)	0.1825 (5)	3.7 (1)
C3	0.0981 (9)	0.5043 (4)	0.3619 (5)	4.0 (1)
C4	0.4325 (8)	0.4458 (5)	0.3198 (5)	4.2 (1)
C5	−0.234 (1)	0.2370 (4)	−0.0578 (7)	6.9 (2)
C6	0.011 (1)	0.2853 (4)	−0.2145 (6)	6.0 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{\mathrm{equiv}} = 8\pi^2/3$ × trace of the orthogonalized U tensor.

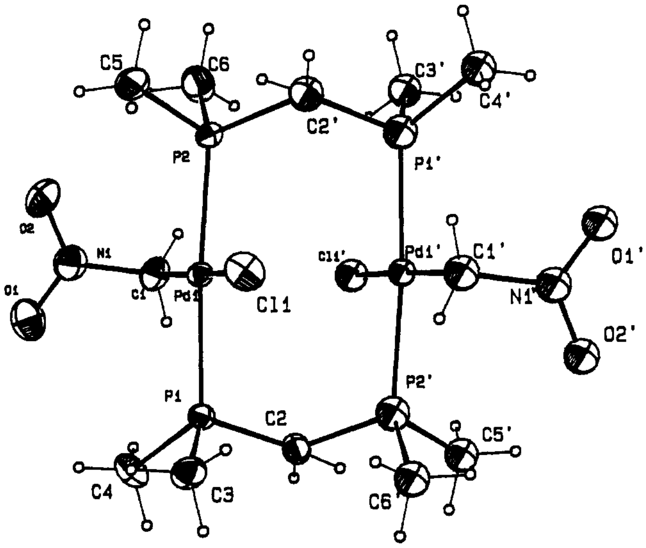

Figure 1. ORTEP diagram of $[Pd_2Cl_2(CH_2NO_2)_2(\mu\text{-dmpm})_2]$ (**6**) showing 50% probability ellipsoids.

Table III. Selected Bond Lengths (Å) and Angles (deg) for 6[a]

Pd1–Cl1	2.364 (2)	P2–C2	1.835 (5)
Pd1–P1	2.319 (1)	P2–C5	1.811 (7)
Pd1–P2	2.310 (1)	O1–N1	1.212 (7)
Pd1–C1	2.066 (6)	O2–N1	1.214 (7)
P2–C6	1.818 (7)	N1–C1	1.460 (7)
P1–C3	1.797 (6)	P1–C2	1.818 (6)
P1–C4	1.806 (6)		
Cl1–Pd1–P1	91.02 (5)	Pd1–P2–C2	112.9 (2)
Cl1–Pd1–P2	87.77 (6)	Pd1–P2–C5	111.8 (2)
Cl1–Pd1–C1	174.7 (2)	Pd1–P2–C6	120.9 (2)
P1–Pd1–P2	175.64 (5)	C2–P2–C5	101.8 (3)
P1–Pd1–C1	90.5 (2)	C2–P2–C6	104.4 (3)
P2–Pd1–C1	91.1 (2)	C5–P2–C6	102.9 (3)
Pd1–P1–C2	108.7 (2)	O1–N1–O2	120.9 (5)
Pd1–P1–C3	116.2 (2)	O1–N1–C1	118.9 (5)
Pd1–P1–C4	121.6 (2)	O2–N1–C1	120.0 (5)
C2–P1–C3	108.3 (3)	Pd1–C1–N1	109.1 (4)
C2–P1–C4	100.2 (3)	P1–C2–P2	118.3 (3)
C3–P1–C4	100.1 (3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

formed as a byproduct. ^1H NMR studies suggest that the transformation of **5** to **6** may indeed be accompanied by H_2 evolution. Thus, addition of 20 μL of protionitromethane to solid $[Pd_2Cl_2(\mu\text{-dmpm})_2]$ in an NMR tube under argon followed, after 1 h, by addition of deuterionitromethane allowed a ^1H NMR spectrum to be obtained that exhibited a weak singlet at 4.51 ppm among the spinning side bands of the protionitromethane. For comparison, bubbling H_2 gas into an NMR tube containing CD_3NO_2 allows observation of the molecular hydrogen resonance at 4.51 ppm. This resonance vanishes upon purging with argon for a few minutes, and similarly, storing the sample of $[Pd_2Cl_2(\mu\text{-dmpm})_2]/CD_3NO_2/CH_3NO_2$ for 12 h at room temperature causes the signal at 4.51 ppm to disappear as hydrogen permeates from the sample. Further evidence for hydrogen evolution was sought through trapping reactions utilizing $[IrCl(CO)(PPh_3)_2]$ as a hydrogen trap. Direct addition of $[IrCl(CO)(PPh_3)_2]$ to $[Pd_2Cl_2(\mu\text{-dmpm})_2]$ in CH_3NO_2 cannot be employed to probe for hydrogen evolution since the iridium and palladium complexes react under these conditions. However, hydrogen production could be investigated by separating the components. Thus, a small flask containing $[Pd_2Cl_2(\mu\text{-dmpm})_2]$ in CH_3NO_2 was connected via a glass line to an NMR tube of $[IrCl(CO)(PPh_3)_2]$ in CD_2Cl_2 and the system sealed. After storage at 0 °C for 2 weeks, the NMR tube was cut from the sealed system and the hydride region was examined by ^1H NMR spectroscopy in order to investigate whether or not sufficient H_2 evolution from the $[Pd_2Cl_2(\mu\text{-dmpm})_2]/CH_3NO_2$ compartment had occurred to allow diffusion into the [IrCl(CO)(PPh$_3$)$_2$]/CD$_2$Cl$_2$ compartment and reaction to produce the known hydride, [IrH$_2$Cl(CO)(PPh$_3$)$_2$]. Indeed, weak signals were observed at −7.02 and −18.34 ppm, which suggest the presence of low levels of [IrH$_2$Cl(CO)(PPh$_3$)$_2$] in solution.[5] Additionally, a triplet at −15.28 ppm ($^2J_{P,H}$ = 11.4 Hz) was observed, which may be indicative of the presence of [IrHCl$_2$(CO)(PPh$_3$)$_2$] in solution.[6] The origin of this product is obscure but may be related to the presence of acidic impurities in the CD$_2$Cl$_2$ employed. Attempts to confirm the presence of these iridium hydrides by ^{31}P{^{1}H} NMR spectroscopy failed due to their very low concentrations.

In addition to the use of trapping experiments we sought to detect evolved hydrogen in the gas phase above a solution of [Pd$_2$Cl$_2$(μ-dmpm)$_2$] in CH$_3$NO$_2$ by Raman spectroscopy and by gas chromatography using a Porapak Q column. Neither of these experiments produced any positive evidence for hydrogen evolution. The NMR experiments are certainly suggestive of H$_2$ evolution in the reaction of [Pd$_2$Cl$_2$(μ-dmpm)$_2$] with CH$_3$NO$_2$, but some ambiguity clearly remains. The long time period over which the reaction occurs (several weeks near 0 °C) hinders definitive experiments.

Interestingly, the complex [Pd$_2$Cl$_2$(μ-dppm)$_2$] does not react with nitromethane under conditions comparable to those employed for the dmpm complex, **5**, indicating that the reaction of this substrate with d^9–d^9 dipalladium systems is sensitive to the steric and electronic properties of the ligand set.[7]

Given the differences in reactivity toward nitromethane of the d^9–d^9 dipalladium and digold complexes, **5** and **1**, it will be of interest to compare the reactions of the d^{10}–d^{10} dipalladium complexes, [Pd$_2$(diphosphine)$_3$], with those already reported for the d^{10}–d^{10} digold complex, **4**. Studies in this area are underway.

Experimental Section

The compounds [Pd$_2$Cl$_2$(μ-dppm)$_2$][8] and [IrCl(CO)(PPh$_3$)$_2$][9] were prepared by literature routes. [Pd$_2$Cl$_2$(μ-dmpm)$_2$] was prepared by ligand exchange of [Pd$_2$Cl$_2$(μ-dppm)$_2$] with dmpm.[10] NMR measurements were made on Varian VXR-400 and JEOL FX-90Q NMR spectrometers. IR measurements were made on a Nicolet 5DX FTIR spectrometer. Raman measurements were made by Dr. E. W. Findsen of this Department using equipment assembled in house. GC measurements were made on a Hewlett-Packard 5890 chromatograph equipped with a Porapak Q column.

Preparation of [Pd$_2$Cl$_2$(CH$_2$NO$_2$)$_2$(μ-dmpm)$_2$] (6). [Pd$_2$Cl$_2$(μ-dmpm)$_2$] (160 mg) was dissolved in CH$_3$NO$_2$ (12 mL), and the solution was stored in the freezer compartment of a refrigerator (ca. 0 °C) for 15 weeks, during which time light yellow crystals of **6** precipitated. Filtration and air-drying allowed isolation of **6** in 30% yield.

Crystallographic Studies. Crystal data are collected in Table I. Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied. The structure was solved by the Patterson heavy-atom method, which revealed the position of one palladium atom. The remaining atoms were located via successive difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained as riding atoms. Final values of R = 0.032 and R_w = 0.039 were obtained. All calculations were performed on a VAX 11/750 computer using SDP-VAX. Full details are included in the supplementary material.

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Registry No. 5, 89178-59-6; 6, 134967-74-1; [Pd$_2$Cl$_2$(μ-dppm)$_2$], 64345-29-5; MeNO$_2$, 75-52-5.

Supplementary Material Available: A complete textural description of the data collection and refinement and tables of crystallographic data and thermal parameters (7 pages); a table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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[5] Literature values are −7.3 and −18.4 ppm in CH$_2$Cl$_2$ solution, see: Taylor, R. C.; Young, J. F.; Wilkinson, G. *Inorg. Chem.* **1966**, 5, 20.

[6] The same triplet is observed when [IrCl(CO)(PPh$_3$)$_2$] in CD$_2$Cl$_2$ is treated with concentrated HCl. The complex [IrHCl$_2$(CO)(PPh$_3$)$_2$] has been synthesized previously by the reaction of [IrCl(CO)(PPh$_3$)$_2$] with HCl, see: Vaska, L *J. Am. Chem. Soc.* **1966**, *88*, 4100.

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Oxidative Addition of Carboxylic Acid Anhydrides to Rhodium(I) Phosphine Complexes To Produce Novel Rhodium(III) Acyl Derivatives

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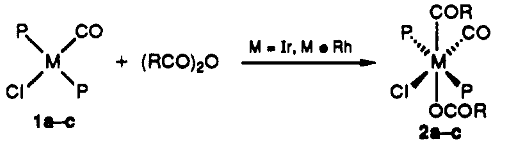
Summary: Oxidative addition of carboxylic acid anhydrides to low-valent Rh(I) phosphine compounds takes place under mild conditions to produce the corresponding Rh(III) acyl complexes, in which the carboxylate ligand is bidentate in nature.

The oxidative addition of acetic anhydride to the Ir(I) complex **1a** has been reported to proceed under mild conditions and produce the respective stable Ir(III) acyl derivative **2a** (eq 1).[2] While a few examples of reactions of Rh(I) compounds with anhydrides have been reported[3a–c] and in one case the corresponding oxidative-addition



1a–c **2a–c** (1)

a: M = Ir; P = Me$_2$PhP; R = Me
b: M = Rh; P = Ph$_3$P; R = Et
c: M = Rh; P = Me$_2$PhP; R = Et

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[1] Present address: Exxon Chemical Co., Basic Chemicals Technology, P.O. Box 4900, Baytown, TX 77522-4900.

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