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Supplementary Material Available: Tables of elemental analyses, ^1H and ^{13}C NMR data of $LCo(DH)_2CH(CN)CH_2CN$, bond lengths and angles, H atomic parameters, and anisotropic temperature factors and two figures related to the NMR discussion (7 pages); a listing of structure factors (22 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of Novel Palladium(II) Cyclometalated Complexes of 2-Vinylpyridine Derivatives[1a]

George R. Newkome,* Kevin J. Theriot, Barry K. Cheskin,[1b] David W. Evans,[1b,c] and Gregory R. Baker

Department of Chemistry, University of South Florida, Tampa, Florida 33620

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Novel dimeric cyclometalated complexes of 2-vinylpyridine derivatives [e.g., bis(μ-chloro)bis[2-(2-pyridinyl)-3-acetoxypropenyl-*C*,*N*]dipalladium(II)] that possess Pd–C_{sp^2} σ-bonds have been synthesized and characterized by ^1H and ^{13}C NMR spectroscopy. The pyridine and PPh_3 monomers of these complexes were also synthesized, and the existence of the Pd–C σ-bond was proven by an X-ray crystal structure determination of chloro[2-(2-pyridinyl)-3-acetoxypropenyl-*C*,*N*](triphenylphosphine)palladium(II) ($PdClC_{28}H_{25}NO_2P$): a = 9.5939 (10) Å, b = 29.702 (4) Å, c = 9.0964 (16) Å, β = 100.045 (11)°, monoclinic, $P2_1/c$, Z = 4.

Introduction

Although five-membered N,C-cyclometalated σ complexes, where the carbon bonded to the metal is sp^2 hybridized, are well-known, examples with pyridine as the N donor are rather limited[2] and most reports have used 2-arylpyridines. Considering the greater reactivity of an isolated carbon–carbon double bond compared to an aryl moiety, cyclometalation of 2-vinylpyridine (2-vp) should be more facile than 2-phenylpyridine, for example. However, to the best of our knowledge, reports of cyclometalated 2-vp (or derivatives) are also limited.[3] This can be rationalized by considering the accepted mechanism of the reaction. The first step is the straightforward formation of the M–N bond. Next, electrophilic attack of the metal on the double bond (2-vp) or aromatic ring (2-arylpyridine) occurs, generating a positive charge on the carbon α to the pyridine. In 2-arylpyridines, this positive charge is stabilized by delocalization in the carbocyclic ring, but in 2-vp, delocalization would result in disruption of the aromaticity of the pyridine ring. Thus, the charge resides mostly on the α-carbon, which is a secondary carbocation possessing an electron-withdrawing group (pyridine), which destabilizes the cation even further. To circumvent this, a very electrophilic metal must be used or the cation intermediate must be stabilized by suitable electron-donating substituents (R). The final step in the mechanism is deprotonated at the β-position to regenerate a double bond.

We tested this hypothesis by studying the cyclometalation reactions of suitably α-substituted 2-vinylpyridines with $PdCl_2$ and found that cyclometalation readily occurs, at 25 °C, to give the dimeric complexes $\{Pd[pyC(R)=CH](\mu\text{-}Cl)\}_2$ (R = CH_2OH, CH_2OAc).[4]

Results and Discussion

Dichloropalladium(II) does not readily undergo cyclometalation with 2-vp because of the formation of an intermediate secondary carbocation (see Figure 1). To circumvent this problem, the α-substituted derivative **1** was chosen for cyclometalation for two reasons: (1) α-substitution would generate a more stable tertiary cation in the intermediate; (2) a functionalized α-substituent would allow such uses as polymer functionalization, synthesis of dinuclear complexes, and easy ligand modification.

Ligand **1a** was easily synthesized by the method of Bohlmann et al.[5] from the commercially available[6] 2-(2-pyridinyl)-1,3-propanediol. Treatment of the propanediol with acetic anhydride at reflux for 6 h yielded (94%) **1a**,

(1) (a) Chemistry of Heterocyclic Compounds Series. Part 141. For Part 140 see: Fronczek, F. R.; Kahwa, I.; Lu, S.; Newkome, G. R.; Ollino, M. A.; Pitts, W. D.; Sittattrakul, A.; Wang, J.-C.; Watkins, S. F. *Acta Crystallogr.* **1988**, *C44*, 933. (b) Department of Chemistry, Louisiana State University, Baton Rouge, LA 70893. (c) Current address: Chemistry Department, Presbyterian College, Clinton, SC 29325.

(2) For reviews see: (a) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327. (b) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73. (c) Constable, E. C. *Polyhedron* **1984**, *3*, 1037. (d) Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E. *Chem. Rev.* **1986**, *86*, 451.

(3) (a) Foot, R. J.; Heaton, B. T. *J. Chem. Soc., Chem. Commun.* **1973**, 838. (b) Foot, R. J.; Heaton, B. T. *J. Chem. Soc., Dalton Trans.* **1979**, 295. (c) Bruce, M. I.; Goodall, B. L.; Matsuda, I. *Aust. J. Chem.* **1975**, *28*, 1259. (d) Burgess, K.; Holden, H. D.; Johnson, B. F. G.; Lewis, J.; Hursthouse, M. B.; Walker, N. P. C.; Deeming, A. J.; Manning, P. J.; Peters, R. *J. Chem. Soc., Dalton Trans.* **1985**, *85*. (e) Heaton, B. T.; McCaffrey, D. J. A. *J. Chem. Soc., Chem. Commun.* **1973**, 817. (f) Heaton, B. T.; Timmins, K. J. *J. Organomet. Chem.* **1978**, *152*, 125.

(4) Under the same conditions, 2-vinylpyridine does not undergo cyclometalation.

(5) Bohlmann, Von F.; Ottawa, N.; Keller, R. *Ann. Chem.* **1954**, *587*, 162.

(6) 2-(2-Pyridyl)-1,3-propanediol was purchased from Aldrich Chemical Co., Milwaukee, WI, but is no longer available. See ref 5.

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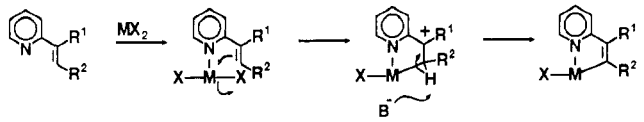
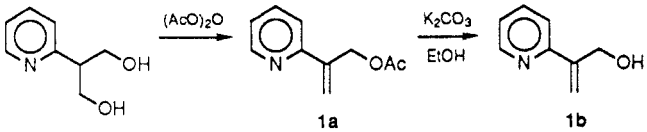


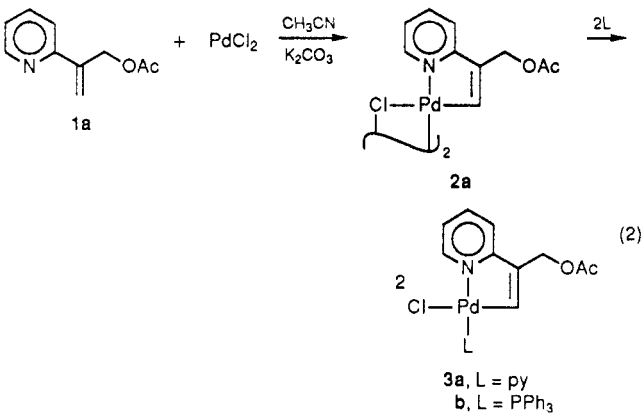
Figure 1. Mechanism for cyclometalation of 2-vinylpyridine with MX_2.

which underwent facile transesterification with anhydrous K_2CO_3 in absolute EtOH to give (57%) **1b** (eq 1).



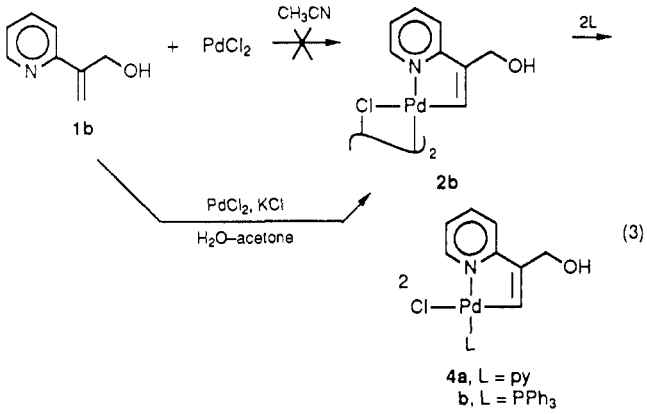
(1)

Cyclometalation of **1a** with $PdCl_2$ occurred at 25 °C in CH_3CN to give (47%) the chloro-bridged dimer **2a**; addition of K_2CO_3 increased the yield to 67%. The 2:1 complex $PdCl_2(\mathbf{1a})_2$ could not be obtained under these conditions by using 2 equiv of ligand. Dimer **2a** reacted, as expected, with either pyridine or PPh_3 to give monomers **3** (eq 2).



(2)

Although reaction of **1b** with $PdCl_2$ in CH_3CN *did not* give $\{Pd(py\text{-}2\text{-}C(CH_2OAc)=CH)(\mu\text{-}Cl)\}_2$ (**2b**), the use of K_2PdCl_4 (generated in situ) in H_2O–acetone did yield (96%), dimer **2b**, which also reacted with either pyridine or PPh_3 to give monomers **4** (eq 3).



(3)

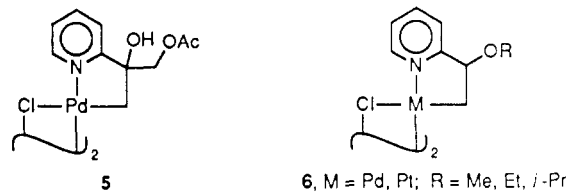
Because of the high yield (96%) of **2b** when the reaction was conducted in H_2O–acetone, these conditions were used on ligand **1a** to give (74%) dimer **2a**. When excess **1a** was used, the yield was generally lower (50–60%). Dimer **5** was sometimes isolated under these conditions in varying (10–40%) yields. A similar product was reported[7] when

(7) Kasahara, A.; Tanaka, K.; Izume, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1702.

Table I. Crystal Data for Complex 3b

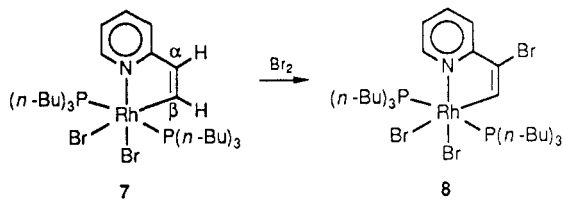
formula	$PdClC_{28}H_{25}NO_2P$	scan rate, deg/min	0.91–4
		precision	$I \approx 25\sigma(I)$
formula wt	580.31	max scan, s	60
cryst syst	monoclinic	no. of unique data	4783
space group	$P2_1/c$	no. of obsd data	3752
a, Å	9.5939 (10)	no. of variables	341
b, Å	29.702 (4)	R	0.0355
c, Å	9.0964 (16)	R_w	0.0357
β, deg	100.045 (11)	max residual, e/Å^3	0.43
V, Å^3	2552.4	color	orange
d, g cm^{-3}	1.510	temp, °C	24
Z	4		
$\mu_{Mo K\alpha}$, cm^{-1}	1.98		
min trans, %	93.45		
cryst size, mm	0.42 × 0.28 × 0.12		
θ limits, deg	$1 < \theta < 25$		

2-vp was reacted with Na_2MCl_4 (M = Pd, Pt) in various alcohols to give complexes **6**.



5 **6**, M = Pd, Pt; R = Me, Et, *i*-Pr

Foot and Heaton reported[3a,b] the synthesis of complex **8** by reaction of the 2-vp complex **7** with Br_2. When dimer **2a** was reacted with Br_2, an inseparable mixture of oxidation products was obtained.



7 **8**

Proton NMR Spectroscopy. A comparison of the chemical shifts of the 6-pyridinyl protons in **1**–**4** shows a gradual *downfield* shift when the ligands (ca. 8.5 ppm) are compared to the dimers (ca. 8.8 ppm), which are in turn compared to the monomers (9.03–9.36 ppm). These shifts are probably due to the difference in the electron-withdrawing effects of the metal centers on the pyridine rings as well as the trans effects in the complexes.

The most important shifts in the ^1H NMR spectra are those of the vinyl protons. For the allyl acetate and alcohol ligands these resonances appear at 5.56/5.99 and 5.50/5.78 ppm, respectively. The analogous cyclometalated complexes show the disappearance of one resonance and the collapse to a singlet of the other resonance, which is shifted *downfield* relative to the analogous ligand. The allyl acetate complexes range from 6.63 to 7.04 ppm and the allyl alcohol complexes range from 6.20 to 6.80 ppm. These shifts are in the same range as those observed by Foot and Heaton[3a,b] for complexes related to **7** and again are due to an electron-withdrawing effect of the metal on the vinyl carbons. The only other shifts are a slight *upfield* shift (ca. 0.4 ppm) of the allyl CH_2 protons observed on complexation.

Carbon-13 NMR Spectroscopy. The only extreme shifts in the ^{13}C NMR spectra are those of the β-alkenyl carbons, which exhibit large downfield shifts upon complexation from ca. 116 ppm in the ligands to ca. 168 ppm in the complexes; similar shifts are observed in the related complexes **7**.[3a,b] All other shifts are similar to those observed in the ligands.

Table II. Important Bond Lengths (Å) and Bond Angles (deg) for 3b

	Distances		
Pd(1)-Cl(1)	2.372 (1)	C(1)-C(2)	1.328 (8)
Pd(1)-C(1)	1.982 (5)	C(2)-C(01)	1.462 (7)
Pd(1)-N(1)	2.111 (4)	C(01)-N(1)	1.361 (7)
Pd(1)-P(1)	2.252 (1)		
	Angles		
Cl(1)-Pd(1)-C(1)	172.3 (2)	Pd(1)-C(1)-C(2)	116.8 (4)
Cl(1)-Pd(1)-N(1)	93.4 (1)	C(1)-C(2)-C(01)	117.0 (5)
Cl(1)-Pd(1)-P(1)	98.02 (4)	Pd(1)-N(1)-C(01)	112.8 (3)
C(1)-Pd(1)-N(1)	79.4 (2)	Pd(1)-P(1)-C(11)	120.2 (1)
C(1)-Pd(1)-P(1)	89.3 (2)	Pd(1)-P(1)-C(21)	111.4 (2)
N(1)-Pd(1)-P(1)	168.2 (1)	Pd(1)-P(1)-C(31)	111.9 (2)

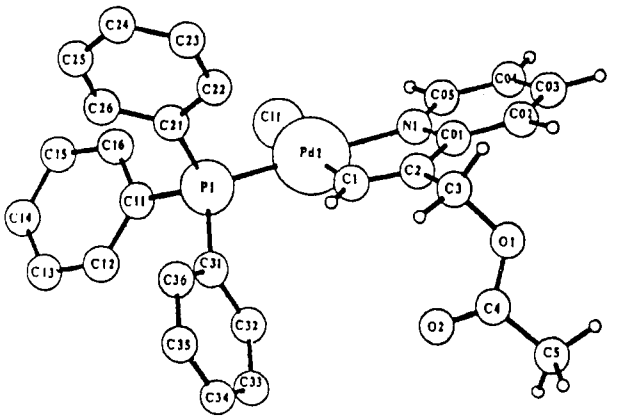


Figure 2. PLUTO drawing of **3b**.

Structure Determination. To confirm the existence of the Pd–C bond an X-ray crystal structure determination of **3b** was undertaken. Crystal data and experimental details are listed in Table I, and important bond distances and angles are given in Table II. The non-hydrogen coordinates are given in Table III, and a PLUTO drawing with the numbering scheme is shown in Figure 2. The Pd–Cl distance [2.372 (1) Å] is longer than expected due to the trans effect of the C_{sp^2} moiety. The Pd–P, Pd–N, and Pd–C distances are all within the normal range for Pd(II) complexes [2.252 (2), 2.111 (4), and 1.982 (5) Å, respectively]. The coordination sphere about Pd(II) is planar (maximum deviation 0.06 Å) with the following cis-coordination angles: Cl(1)–Pd(1)–N(1), 93.4 (1)°; Cl(1)–Pd(1)–P(1), 98.02 (4)°; C(1)–Pd(1)–N(1), 79.4 (2)°; C(1)–Pd(1)–P(1), 89.3°. The chelate atoms [Pd, C(1), C(2), C(01), N(1)] lie in a plane (maximum deviation 0.015 Å) that forms a dihedral angle to the coordination atoms plane of 2.9°, which decreases to 1.3° with the pyridine carbons included in the least-squares plane calculation. The C(1)–C(2) distance is 1.328 (8) Å, indicating the presence of the carbon–carbon double bond.

Conclusion

Novel dimeric cyclometalated complexes of 2-vinylpyridine derivatives and their pyridine and PPh_3 monomers that possess Pd–C_{sp^2} σ-bonds, in which the sp^2 carbon is part of a vinyl (allyl) system rather than in an aromatic ring, have been synthesized and characterized by ^1H NMR and ^{13}C NMR spectroscopy. An X-ray crystal structure determination of one of the monomers proved the existence of the Pd–C σ-bond.

Experimental Section

General Comments. All melting points were taken in open capillary tubes with either a Thomas-Hoover Unimelt or a Gallenkamp melting point apparatus and are uncorrected. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions, except where noted. Deuterated solvent residues were used as internal standards [$CHCl_3$, 7.27 (^1H) and 77.0 (^{13}C) ppm; Me_2SO, 2.49 (^1H) and 39.5 (^{13}C) ppm] and chemical shift values (δ) are reported in parts per million (ppm) downfield from tetramethylsilane (Me_4Si). Mass spectra (MS) data (70 eV) were determined by H. Land on a Hewlett-Packard HP5895 GC/mass spectrometer. Infrared spectra (IR) were recorded on IBM IR/38 Fourier transform infrared spectrophotometer. Elemental analyses were conducted by either Galbraith Laboratories, Inc. (Knoxville, TN), or M-H-W Laboratories (Phoenix, AZ). "Dry column" flash chromatography was performed by the method of Harwood[8] using preparative grade silica gel (Brinkman PF-254-366) and the eluants specified.

Unless otherwise noted, all reagents and solvents utilized were of reagent grade, and no further purification was undertaken.

X-ray Data Collection. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation (λ = 0.710 73 Å) and a graphite monochromator, by ω–2θ scans of variable speed designed to yield equal relative precision for all significant data. A maximum of 60 seconds was placed on the time allowed for scanning a single reflection. Crystal data and experimental details are listed in Table I. One quadrant of data was measured for each crystal within the specified angular limits.

Structures were solved by heavy-atom methods and refined by full-matrix least-squares methods, treating non-hydrogen atoms anisotropically. Aromatic hydrogen atom positions were calculated and thermal parameters refined while the vinyl and methylene hydrogens were located by difference maps and included as fixed contributions; the methyl hydrogens were located by the two best

Table III. Non-Hydrogen Coordinates (×10⁴) and Isotropic Thermal Parameters (×10³) for 3b

atom	X	Y	Z	U,[a] Å²
Pd(1)	1838.4 (4)	1537.7 (1)	2675.8 (4)	39.1 (1)
Cl(1)	162.5 (14)	1191.2 (5)	790.8 (16)	53.7 (5)
C(1)	3159 (6)	1905 (2)	4114 (6)	47 (2)
C(2)	2860 (6)	2340 (2)	4192 (6)	49 (2)
C(3)	3762 (8)	2662 (2)	5218 (7)	63 (2)
O(1)	4355 (4)	3013 (1)	4398 (5)	64 (2)
C(4)	5581 (7)	2941 (3)	3999 (8)	74 (3)
O(2)	6197 (6)	2592 (2)	4244 (9)	147 (4)
C(5)	6106 (9)	3322 (3)	3174 (10)	105 (4)
N(1)	881 (4)	2178 (1)	2321 (5)	45 (2)
C(01)	1577 (5)	2501 (2)	3227 (6)	49 (2)
C(02)	1056 (7)	2940 (2)	3181 (7)	63 (2)
C(03)	−160 (7)	3040 (2)	2180 (9)	79 (3)
C(04)	−839 (7)	2716 (2)	1273 (9)	74 (3)
C(05)	−298 (6)	2284 (2)	1391 (7)	57 (2)
P(1)	3093.5 (13)	919.0 (4)	3490.6 (14)	37.5 (4)
C(11)	2877 (5)	403 (2)	2392 (5)	36 (2)
C(12)	4031 (5)	187 (2)	1964 (6)	45 (2)
C(13)	3873 (6)	−224 (2)	1217 (6)	52 (2)
C(14)	2564 (6)	−426 (2)	901 (6)	48 (2)
C(15)	1409 (5)	−213 (2)	1341 (6)	46 (2)
C(16)	1557 (5)	198 (2)	2060 (6)	44 (2)
C(21)	2722 (5)	734 (2)	5285 (5)	41 (2)
C(22)	2457 (7)	1049 (2)	6329 (7)	68 (3)
C(23)	2224 (8)	911 (2)	7725 (7)	83 (3)
C(24)	2167 (5)	461 (2)	8067 (6)	57 (2)
C(25)	2393 (6)	151 (2)	7042 (6)	58 (2)
C(26)	2666 (6)	283 (2)	5661 (6)	50 (2)
C(31)	5001 (5)	1023 (2)	3778 (6)	42 (2)
C(32)	5541 (6)	1252 (2)	2659 (6)	59 (2)
C(33)	6966 (7)	1320 (3)	2779 (8)	77 (3)
C(34)	7882 (6)	1170 (2)	4025 (8)	68 (3)
C(35)	7374 (6)	945 (2)	5131 (7)	61 (2)
C(36)	5931 (5)	871 (2)	5012 (6)	46 (2)

[a] Equivalent isotropic thermal factor: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, UK; Vol. 4, p 316.

(8) Harwood, L. M. *Aldrichimica Acta* **1985**, *18*, 25.

peaks in the difference map and the third then calculated, after which the third was fixed and the other two were calculated and all three then remained fixed throughout the refinement. Final *R* factors and residual electron densities are given in Table I; coordinates are listed in Table III.

2-(2-Pyridinyl)-3-acetoxypropene (1a). A stirred solution of 2-(2-pyridinyl)-1,3-propanediol[6] (10.36 g, 6.77 mmol) in Ac_2O (75 mL) was refluxed for 6 h. The Ac_2O was removed in vacuo to give a thin oil, which was distilled under reduced pressure to give (94%) **1a**,[5,9] as a colorless liquid: 11.27 g; bp 105–115 °C (1 mmHg) [lit.[5] bp 120–130 °C (3 mmHg)]; ^{1}H NMR δ 2.09 (s, CH_3, 3 H), 5.16 (d, CH_2, J = 1.4 Hz, 1 H), 5.56 (dd, C$H_{cis\text{-}py}$, ^2J = 0.9, ^4J = 1.4 Hz, 1 H), 5.99 (d, C$H_{trans\text{-}py}$, ^2J = 0.9 Hz, 1 H), 7.18 (ddd, 5-py *H*, $J_{4,5}$ = 7.0, $J_{5,6}$ = 4.8, $J_{3,5}$ = 1.7 Hz, 1 H), 7.42–7.55 (m, 3-py *H*, 1 H), 7.58–7.79 (m, 4-py *H*, 1 H), 8.58 (ddd, 6-py *H*, $J_{5,6}$ = 4.8, $J_{4,6}$ = 1.7, $J_{3,6}$ = 1.0 Hz, 1 H); ^{13}C NMR δ 20.8 (*C*H$_3$), 64.6 (*C*H$_2$), 117.1 (=*C*H$_2$), 120.2 (*C*(3)), 122.7 (*C*(5)), 136.5 (*C*(4)), 142.6 (=*C*R$_2$), 149.2 (*C*(6)), 156.0 (*C*(2)), 170.9 (*C*O); MS, *m*/*z* 177 (2), 134 (100), 78 (15), 43 (19).

2-(2-Pyridinyl)-3-hydroxypropene (1b). A stirred solution of 2-(2-pyridinyl)-3-acetoxypropene (490 mg, 2.77 mmol) and anhydrous K_2CO_3 (300 mg, 2.16 mmol) in EtOH (50 mL) was refluxed for 15 h. After concentration, the resulting solid was extracted with CH_2Cl_2, the solvent removed in vacuo, and the resulting oil distilled under reduced pressure to give (71%) pure **1b**:[9] 213 mg; bp 135–145 °C (1 mmHg); ^{1}H NMR δ 4.60 (s, CH_2, 1 H), 5.50 (s, C$H_{cis\text{-}py}$, 1 H), 5.78 (s, C$H_{trans\text{-}py}$, 1 H), 7.18 (ddd, 5-py *H*, $J_{4,5}$ = 6.8, $J_{5,6}$ = 4.8, $J_{3,5}$ = 2.0 Hz, 1 H), 7.55–7.82 (m, 3-py *H*, 1 H), 7.63–7.77 (m, 4-py *H*, 1 H), 8.50 (ddd, 6-py *H*, $J_{5,6}$ = 4.8, $J_{4,6}$ = $J_{3,6}$ = 1.2 Hz, 1 H); ^{13}C NMR δ 65.6 (*C*H$_2$), 115.8 (=*C*H$_2$), 120.1 (*C*(3)), 122.4 (*C*(5)), 136.6 (*C*(4)), 145.9 (=*C*R$_2$), 148.3 (*C*(6)), 157.4 (*C*(2)); MS, *m*/*z* 135 (22), 134 (36), 117 (5), 106 (100), 105 (19), 104 (37), 79 (28), 78 (62).

Bis(μ-chloro)bis[2-(2-pyridinyl)-3-acetoxypropenyl-*C*,*N*]dipalladium(II) (2a). Method A. A solution of $PdCl_2$ (297 mg, 1.67 mmol), allyl acetate **1a** (302 mg, 1.71 mmol), and anhydrous K_2CO_3 (470 mg, 3.40 mmol) in CH_3CN (100 mL) was stirred for 12 h at 25 °C. The solvent was then removed in vacuo, and the resulting solid extracted with $CHCl_3$. After removal of the $CHCl_3$, the mixture was purified by using dry flash[8] chromatography (SiO_2), eluting with $CHCl_3$ to give (67%) **2a**, as light yellow microcrystals: 362 mg; mp >255 °C (dec); ^{1}H NMR (Me$_2$SO-d_6) δ 2.01 (s, CH_3, 3 H), 4.76 (s, CH_2, 2 H), 7.04 (s, C*H*, 1 H), 7.34 (dd, 3-py *H*, $J_{3,4}$ = 7.8, $J_{3,5}$ = 1.4 Hz, 1 H), 7.37 (ddd, 5-py *H*, $J_{5,6}$ = 4.7, $J_{4,5}$ = 7.7, $J_{3,5}$ = 1.4 Hz, 1 H), 8.03 (ddd, 4-py *H*, $J_{4,5}$ = $J_{3,4}$ = 7.7 $J_{4,6}$ = 1.7 Hz, 1 H), 8.85 (bd, 6-py *H*, $J_{5,6}$ = 4.7 Hz, 1 H); ^{13}C NMR (Me$_2$SO-d_6) δ 20.4 (*C*H$_3$), 62.1 (*C*H$_2$), 119.9 (*C*(3)), 122.2 (*C*(5)), 140.9 (*C*(4)), 142.3 (=*C*R$_2$), 150.0 (*C*6), 165.2 (*C*2), 170.1 (*C*O), 171.6 (Pd*C*); IR (KBr) 1732 s (C=O), 1603, 1480 s (C=C, C=N), 1264 s, 1030 (C–O), 826, 776 cm^{-1}. Anal. Calcd for $C_{20}H_{20}N_2Cl_2O_4Pd_2$: C, 37.76; H, 3.17; N, 4.40; Cl, 11.15. Found: C, 37.73; H, 3.18; N, 4.32; Cl, 10.91.

Method B. A solution of allyl acetate **1a** (131 mg, 740 μmol) in acetone (15 mL) was added to a stirred solution of $PdCl_2$ (132 mg, 744 μmol) and KCl (165 mg, 2.21 mmol) in H_2O (10 mL), and the solution was stirred at 25 °C for 12 h. The mixture was then filtered to give (74%) **2a**, as a light yellow solid (176 mg). In some reactions, a byproduct was also isolated (10–40%) and shown to be dimer **5**: mp >280 °C; ^{1}H NMR (Me$_2$SO-d_6) δ 2.00 (s, CH_3, 3 H), 2.18 (d, PdCH_2, ^2J = 9.2 Hz, 1 H), 2.62 (d, PdCH_2, ^2J = 9.2 Hz, 1 H), 4.21 (d, OCH_2, ^2J = 11.1 Hz, 1 H), 4.38 (d, OCH_2, J_{gem} = 11.1 Hz, 1 H), 6.07 (s, O*H*, 1 H), 7.47–7.59 (m, 3,5-py *H*, 2 H), 8.07 (ddd, 4-py *H*, $J_{3,4}$ = $J_{4,5}$ = 7.3 $J_{4,6}$ = 1.4 Hz, 1 H), 8.89 (d, 6-py H, $J_{5,6}$ = 5.5 Hz, 1 H); ^{13}C NMR (Me$_2$SO-d_6) δ 20.1 (*C*H$_3$), 39.1 (Pd*C*H$_2$), 70.4 (*C*H$_2$O), 80.7 (α-*C*), 123.3, 123.6 (*C*(3) and *C*(5)), 138.9 (*C*(4)), 148.5 (*C*(6)), 168.9, 169.1 (*C*(2) and *C*O); IR (KBr) 3468 br (OH), 1738 s (C=O), 1607, 1478 (C=C, C=N), 1250, 1048 (C–O) cm^{-1}. Anal. Calcd for $C_{20}H_{24}N_2Cl_2O_6Pd_2$: C, 35.74; H, 3.60; N, 4.17. Found: C, 35.89; H, 3.63; N, 4.16.

Chloro[2-(2-pyridinyl)-3-acetoxypropenyl-*C*,*N*](pyridine)palladium(II) (3a). Excess pyridine (≈600 mg) was added to a stirred solution of **2a** (63 mg, 0.1 mmol) in CH_2Cl_2 (10 mL), and after stirring for 12 h at 25 °C the solvent was removed. Purification by column chromatography (SiO_2) eluting with CH_2Cl_2 gave (100%) **3a**, as a yellow solid: 80 mg; mp 189–190 °C (dec); ^{1}H NMR δ 2.06 (s, CH_3, 3 H), 4.79 (s, CH_2, 2 H), 6.99 (s, =C*H*, 1 H), 7.05–7.15 (m, 3,5-py *H*, 2 H), 7.44 (dd, 3′-py *H*, $J_{3,4}$ = 7.1, $J_{2,3}$ = 7.1 Hz, 2 H), 7.70–7.95 (m, 4-,4′-py *H*, 2 H), 8.85 (d, 2′-py *H*, $J_{2,3}$ = 7.1 Hz, 1 H), 9.25 (d, 6-py *H*, $J_{5,6}$ = 4.7 Hz, 1 H); ^{13}C NMR δ 20.7 (*C*H$_3$), 62.5 (*C*H$_2$), 118.8 (*C*(3)), 121.0 (*C*(5)), 125.2 (*C*(3′)), 138.0, 138.9 (*C*(4) and C(4′)), 142.2 (=*C*R$_2$), 152.1 (*C*(6)), 153.1 (*C*(2′)), 166.2, 166.9 (*C*2 and Pd–*C*), 170.3 (*C*O); IR (KBr) 1721 (C=O), 1447, 1480 (C=C, C=N), 1223, 1028 (C–O), 830, 760, 696 cm^{-1}. Anal. Calcd for $C_{15}H_{15}N_2ClO_2Pd$: C, 45.36; H, 3.81; N, 7.05. Found: C, 45.22; H, 3.86; N, 7.00.

Chloro[2-(2-pyridinyl)-3-acetoxypropenyl-*C*,*N*](triphenylphosphine)palladium(II) (3b). A solution of **2a** (71 mg, 0.11 mmol) and triphenylphosphine (64 mg, 0.24 mmol) in CH_2Cl_2 (20 mL) was stirred for 18 h at 25 °C. The solvent was then removed to give (95%) **3b**, as a yellow solid: 123 mg; mp 187–188 °C (dec); ^{1}H NMR δ 1.98 (s, CH_3, 3 H), 4.61 (s, CH_2, 2 H), 6.63 (d, =C*H*, $J_{P,H}$ = 19.0 Hz, 1 H), 7.10 (d, 3-py *H*, $J_{3,4}$ = 7.9 Hz, 1 H), 7.19 (dd, 5-py *H*, $J_{4,5}$ = 7.5, $J_{5,6}$ = 4.4 Hz, 1 H), 7.39–7.49 (m, 2,4,6-Ph *H*, 9 H), 7.60–7.78 (m, 3,5-Ph *H* and 4-py *H*, 7 H), 9.36 (t, 6-py *H*, $J_{5,6}$ = $J_{P,H}$ = 4.4 Hz, 1 H); ^{13}C NMR (400 MHz) δ 20.9 (*C*H$_3$) 64.2 (*C*H$_2$), 118.5 (*C*(3)), 121.4 (*C*(5), J_{PC} = 3 Hz), 128.4 (*C*(3′), J_{PC} = 11.1 Hz), 130.2 (*C*(1′), J_{PC} = 52.3 Hz), 130.8 (*C*(4′), J_{PC} = 2.0 Hz), 134.7 (*C*(2′), J_{PC} = 12.1 Hz), 139.2 (*C*(4)), 142.6 (=*C*R$_2$), 150.0 (*C*(6)), 164.3 (*C*(2), J_{PC} = 4.0 Hz), 170.1 (Pd–*C*, J_{PC} = 4.0 Hz), 170.6 (*C*O); IR (KBr) 1742 s (C=O), 1603, 1480 (C=C, C=N), 1435 s (P–C), 1219 s, 1096 (C–O), 750, 694 cm^{-1}. Anal. Calcd for $C_{28}H_{25}NClO_2PPd$: C, 57.95; H, 4.34; N, 2.41. Found: C, 57.80; H, 4.52; N, 2.16.

Bis(μ-chloro)bis[2-(2-pyridinyl)-3-hydroxypropenyl-*C*,*N*]dipalladium(II) (2b). Allyl alcohol **1b** (300 mg, 2.22 mmol) in acetone (5 mL) was added to a stirred solution of $PdCl_2$ (200 mg, 1.13 mmol) and KCl (300 mg, 4.02 mmol) in H_2O (15 mL). After stirring for 16 h at 27 °C, the mixture was filtered and washed with acetone to give (96%) **2b**·H_2O, as a yellow solid: 310 mg; mp 217 °C (dec); ^{1}H NMR (Me$_2$SO-d_6) δ 4.16 (s, CH_2, 2 H), 6.80 (s, =C*H*, 1 H), 7.27–7.55 (m, 3,5-py *H*, 2 H), 8.00 (ddd, 4-py *H*, $J_{3,4}$ = $J_{4,5}$ = 7.8, $J_{4,6}$ = 1.7 Hz, 1 H), 8.83 (d, 6-py *H*, $J_{5,6}$ = 4.5 Hz, 1 H); ^{13}C NMR (Me$_2$SO-d_6) δ 60.4 (*C*H$_2$), 120.4 (*C*(3)), 121.9 (*C*(5)), 140.6 (*C*(4)), 148.1 (*C*(6)), 149.9 (α-*C*), 166.3 (Pd–*C*), 166.4 (*C*(2)); IR (KBr) 3337 br (OH), 1599 s, 1482 s (C=C, C=N), 1080 (C–O), 822, 762 cm^{-1}. Anal. Calcd for $C_{16}H_{16}N_2Cl_2O_2Pd_2$·$H_2O$: C, 33.71; H, 3.18; N, 4.91. Found: C, 33.81; H, 3.42; N, 4.78.

Chloro[2-(2-pyridinyl)-3-hydroxypropenyl-*C*,*N*](pyridine)palladium(II) (4a). An excess of pyridine was added to a stirred suspension of **2b** (85 mg, 0.15 mmol) in $CHCl_3$ (25 mL). After stirring for 12 h at 25 °C, the solvent was removed and the resulting solid was purified on a SiO_2 column, eluting with $CHCl_3$ to give (66%) **4a**, as a yellow solid: 72 mg; mp 138–141 °C; ^{1}H NMR δ 1.56 (t, O*H*, J = 5.8 Hz, 1 H), 4.36 (d, CH_2, J = 5.8 Hz, 2 H), 6.83 (s, =C*H*, 1 H), 7.07 (ddd, 5-py *H*, $J_{4,5}$ = 7.3, $J_{5,6}$ = 5.6, $J_{3,5}$ = 1.4 Hz, 1 H), 7.18–7.85 (m, 3,3′-py *H*, 3 H), 7.88–7.96 (m, 4,4′-py *H*, 2 H), 8.88 (d, 2′-py *H*, $J_{2,3}$ = 5.6 Hz, 2 H), 9.25 (d, 6-py *H*, $J_{5,6}$ = 5.1 Hz, 1 H); ^{13}C NMR δ 61.4 (*C*H$_2$), 119.4 (*C*(3)), 120.6 (*C*(5)), 125.1 (*C*(3′)), 138.0, 138.7 (*C*(4) and *C*(4′)), 147.0 (α-*C*), 151.4 (*C*(6)), 152.9 (*C*(2′)), 162.0 (*C*(2)), 166.2 (Pd–*C*); IR (KBr) 3376 br (OH), 1601 s, 1480 s, 1449 s (C=C, C=N), 1084 (C–O), 820, 758, 698 cm^{-1}. Anal. Calcd for $C_{13}H_{13}N_2ClOPd$: C, 43.97; H, 3.69; N, 7.89. Found: C, 43.90; H, 3.76; N, 7.84.

Chloro[2-(2-pyridinyl)-3-hydroxypropenyl-*C*,*N*](triphenylphosphine)palladium(II) (4b). Triphenylphosphine (83 mg, 0.317 mmol) was added to a stirred solution of **2b** (87 mg, 0.16 mmol) in $CHCl_3$ (10 mL). After stirring for 12 h at 25 °C, the solvent was removed to give (90%) **4b**, as a yellow solid: 153 mg; mp 109–112 °C; ^{1}H NMR δ 1.22 (t, O*H*, J = 5.7 Hz, 1 H), 4.17 (d, CH_2, J = 5.7 Hz, 2 H), 6.20 (d, =C*H*, $J_{P,H}$ = 19.2 Hz, 1 H), 7.11–7.41 (m, 2,4,6-Ph *H* and 3,5-py *H*, 11 H), 7.56–7.87 (m, 3,5-Ph *H* and 4-py *H*, 7 H), 9.35 (dd, 6-py *H*, $J_{5,6}$ = $J_{P,H}$ = 4.4 Hz, 1 H); ^{13}C NMR δ 63.1 (*C*H$_2$), 119.4 (*C*(3)), 121.1 (*C*(5)), 128.2 (*C*(3′), J_{PC} = 10.8 Hz), 130.3 (*C*(1′), J_{PC} = 50.1 Hz), 130.6 (*C*(4′)), 134.5 (*C*(2′), J_{PC} = 11.8 Hz), 139.1 (*C*(4)), 148.1 (α-*C*), 149.5 (*C*(6)), 164.7 (*C*(2)), 165.6 (Pd-*C*); IR (KBr) 3422 br (OH), 1601, 1480

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(C=C, C=N), 1435 s (P-C), 1098 (C-O), 746, 694 s cm^{-1}. Anal. Calcd for $C_{26}H_{23}NClOPPd$: C, 58.01; H, 4.31; N, 2.60. Found: C, 58.06; H, 4.57; N, 2.55.

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Supplementary Material Available: Listings of bond distances and angles, H atom coordinates, and thermal parameters (4 pages); a listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

Kinetic Deuterium Isotope Effects on Ligand Migrations in Metal Hydrides. 2[1]

Julia Bracker-Novak, Sharad Hajela, Michael Lord, Minsheng Zhang, and Edward Rosenberg*

Department of Chemistry, California State University, Northridge, California 91330

Roberto Gobetto, Luciano Milone,* and Domenico Osella

Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Via Giuria 7-9, I 10125 Torino, Italy

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Variable-temperature (VT) ^1H and ^{13}C NMR studies of the complexes $(\mu\text{-X})_2Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}(CH_3CH_2)_2C_2)$ (X = H or D) reveal that alkyne migration over the face of the cluster is directly linked to hydride migrations on the metal core as evidenced by a temperature-independent isotope effect (k_{HH}/k_{DD} = 1.7). In a related study of the VT ^{13}C NMR of $(\mu\text{-X})_2M_3(CO)_9(\mu_3\text{-S})$ (X = H or D; M = Ru, Os) the observation of a k_{HH}/k_{DD} = 1.6 for both the osmium and ruthenium complexes demonstrates that the first stage of carbonyl averaging is brought about by hydride migration and not axial-radial exchange of carbonyl groups, a process that occurs only at higher temperatures. The mechanistic implications of these results are discussed in the context of the reactivity of metal clusters and the dynamic properties of the metal-hydrogen bond.

Introduction

In our recent report on the kinetic deuterium isotope effects in ligand migrations we found k_{HH}/k_{DD} = 1.8 for the direct exchange of two hydride ligands in dihydride clusters and k_{HH}/k_{DD} = 1.5 for axial-radial exchange of carbonyl groups at the hydride bridged edge of the complexes $H(\mu\text{-H})Os_3(CO)_{10}L$.[1] Later, we used these results to interpret the observed kinetic deuterium isotope effects (k_{HH}/k_{DD} = 1.7) in the product distributions in the reaction of $H_2O_3(CO)_{10}$ with *tert*-butylacetylene.[2] We proposed that opening of the hydride bridge controlled edge-to-face (i.e., radial-to-axial) alkyne migration in the intermediate alkyne complex $H(\mu\text{-H})Os_3(CO)_{10}$(alkyne) and thereby controlled the observed product distributions. At about the same time Shore et al. noted an isotope effect (k_H/k_D = 1.5) in the bimolecular term of the rate law for the reaction of carbon monoxide with $(\mu\text{-H})M_3(CO)_{11}^-$ (M = Ru, Os) which he also attributed to a rate-controlling opening of the hydride bridge to create a vacant site for coordination of the incoming carbonyl groups.[3] It appears from these results that an understanding of factors controlling ligand migrations in metal clusters is extremely important in understanding their low-temperature reaction chemistry.

Our first observation of a kinetic deuterium isotope effect in metal cluster chemistry came as a result of our investigation of the two-step protonation of $(\mu\text{-H})Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2{}^tBu)$ with protic acids.[4] We found that the kinetic ratios of the two products formed depended upon whether deuterium was present in the starting cluster hydride or in the acid used. We rationalized these observations by invoking a mechanism where hydride migration was directly coupled to alkyne reorientation over the face of the cluster. Depending on the initial location of deuterium on the cluster one of the two possible hydride migrations would be faster, thus favoring the formation of one of the two kinetic products observed. However, at that time we had not established the connectivity between alkyne migration over the face of a trinuclear cluster and edge-to-edge migration of a hydride. In light of our previous results that established the connectivity between axial-radical carbonyl exchange and hydride bridge opening,[1] we thought it would be useful to extend these studies to the case of alkyne migration in a nonreactive system. We report here a VT ^{13}C and ^1H NMR investigation of the complexes $(\mu\text{-X})_2Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}(CH_3CH_2)_2C_2)$[5] (X = H or D) that lends strong support to our previously proposed mechanism[4] and extends the "cog and wheel" view of cluster ligand dynamics to μ_3-alkyne trinuclear cluster systems.

We also report here a VT ^{13}C NMR investigation of the ligand dynamics in $(\mu\text{-X})_2M_3(CO)_9(\mu^3\text{-S})$ (X = H or D; M = Ru, Os) in which the observed kinetic isotope effect differentiates between possible dynamic processes in a system where hydride motion is a "hidden process."[6]

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