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Stable Glucopyranosylpalladium Complexes with *cis*-β-Hydrogen. A Six-Membered Ring Metallocycle with an Oxygen Donor Ligand

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Two stable glucopyranosylpalladium complexes, chloro[1,3-dimethyl-5-(3,4,6-tri-O-acetyl-2-deoxy-α-D-arabinohexopyranosyl)-2,4(1*H*,3*H*)-pyrimidinedionnato] (triphenylphosphine)-palladium and the corresponding triphenylarsine analog, were studied using fast atom bombardment mass spectrometry, ^{1}H, ^{13}C and ^{31}P nuclear magnetic resonance, UV and IR spectroscopy to establish structures for these complexes. The data obtained indicate that the pyranosyl ring is in a chair conformation in which palladium ($C_{2'}$), acetoxy ($C_{3'}$ $C_{4'}$) and acetoxymethyl ($C_{5'}$) are equatorial and 1,3-dimethyl-2,4(1*H*,3*H*) pyrimidinedion-5-yl ($C_{1'}$) is axial. The palladium(II) ion is encompassed in a six-membered ring metallocycle in which $C_{2'}$ of the glucopyranosyl ring and the oxygen of the C_4 carbonyl of the pyrimidinedionyl group occupy adjacent ligand sites. The other two ligand sites on square planar palladium are occupied by triphenylphosphine (or triphenylarsine) *cis* to $C_{2'}$ and *trans* to carbonyl oxygen, and chloride *trans* to $C_{2'}$ and *cis* to oxygen. This stable metallocycle has three unusual features, a *cis*-β-hydrogen, a six-membered Pd-containing ring and an oxygen donor ligand. Its surprising stability is due to conformational barriers to the proper alignment of Pd with pyranosyl ring substituents required for elimination reactions.

Only a few alkylpalladium compounds which possess a *cis*-β-hydrogen have been isolated.[1–3] We have reported[4] the isolation, characterization and some selective reactions of a stable glucopyranosylpalladium compound (*1*), which possesses a β-hydrogen *cis* to palladium. That compound *1* is sufficiently stable to permit isolation and purification** is impressive since, in addition to decomposition by β-hydride elimination[5–9] compound *1* exhibits two other facile decomposition reactions – *anti* elimination of palladium acetate and pyran ring opening (*i.e.* *anti* elimination of palladium alkoxide).[4–8,10] The structural features which account for the unexpected stability of *1* were not elucidated. We now report a more detailed study of the physical and chemical properties of organopalladium compound

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** Attempts to prepare crystals of *1* for X-ray crystallography have been unsuccessful.

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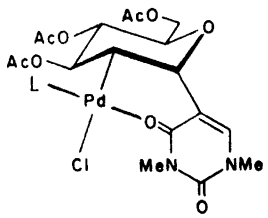
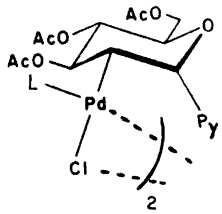




1a L=Ph_3P

2a L=Ph_3As

1b L=Ph_3P

2b L=Ph_3As

Py=1,3-dimethyl-2,4-(1H,3H)-pyrimidinedion-5-yl

1a and a closely related analog *2a* undertaken to gain a fuller understanding of the chemistry of σ-palladium bonded carbohydrate derivates.[11,12]

EXPERIMENTAL

General Comments. Chemicals were used as received. For flash chromatography, silica gel 60 (230–400 mesh ASTM, E. Merck) was used. Columns were eluted using a positive nitrogen pressure. Nuclear magnetic resonance (NMR) spectra were obtained on a JEOL FX 90Q spectrometer from degassed samples kept under nitrogen. ^1H and ^{13}C NMR spectra were referenced to tetramethylsilane. ^{31}P NMR spectra were referenced to phosphoric acid. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. Ultraviolet (UV) spectra were obtained with Cary-15 and perkin-Elmer Lambda 3 spectrophotometers. Mass spectra were obtained using a CEC (DuPont) 21–110 mass spectrometer modified for operation in the fast atom bombardment mode. Microanalysis and melocular weight determinations were performed by Galbraith Laboratories, Knoxville, TN, USA.

Chloro [1,3-dimethyl-5-(3,4,6-tri-0-acetyl-2-deoxy-α-D-arabinohexopyranosyl)-2,4(1H,3H)-pyrimidinedionnato] (triphenylphosphine)palladium (1a).[4] 1,3-Dimethyl-2,4(1*H*,3*H*)-pyrimidinedion-5-yl mercuric acetate[13] (800 mg, 2.01 mmol) was added to a preformed mixture of palladium(II) acetate (450 mg, 2.00 mmol), anhydrous lithium chloride (170 mg, 4.01 mmol), and acetonitrile (50 ml). After five minutes, 3,4,6-tri-O-acetyl-D-glucal[14] (600 mg, 2.21 mmol) was added to the vigorously stirred, slowly darkening solution. The reaction mixture was stirred for 3 d at room temperature and then filtered through Celite. Triphenylphosphine (788 mg, 3.00 mmol) was added to the filtrate and the resulting yellowish solution was allowed to stand under nitrogen for 2 h whereby a precipitate was formed. Filtration followed by evaporation of volatiles *in vacuo* gave an oil which was dissolved in a minimal amount of methylene chloride and applied on a silica gel column. Flash chromatography using ethyl acetate as eluant followed by rechromatography of partially purified fractions afforded an oil which was dissolved in benzene (2 ml). Addition of ether (50 ml) gave 607 mg (38 %) of *1a* as a slightly yellowish amorphous powder, mp. 138 °C. ^1H NMR (89.55 MHz, C_6D_6): δ 1.59, 1.77, 1.79 (OAc's); 2.07 (dt, $J_{1',2'}$=5 Hz, $J_{2',3'}$=12 Hz, $J_{31_{P,H2'}}$=12 Hz, $H_{2'}$); 2.67, 3.23 (NMe's); 3.55 (dt, $J_{4',5'} \approx 10.5$ Hz, $J_{5'6'}=J_{5',6''}$=5 Hz, $H_{5'}$); 4.21 (d, $H_{6'}$, $H_{6''}$); 4.83 (t, $J \approx 10$ Hz, $H_{4'}$); 4.94 (broad, $H_{1'}$); 5.33 (ddd, $J_{31_{P,H3'}}$=2.5 Hz, $H_{3'}$); 6.82 (d, $J_{1',6}$=2 Hz, H_6); 7.24, 8.05–8.20 (Ar).

^{13}C NMR (22.51 MHz, $CDCl_3$): δ 20.36, 20.50, 20.58 (OAc Me's); 29.75 38.04 (NMe's); 36.74, $^2J_{C,P}$=2.5 Hz ($C_{2'}$); 63.12 ($C_{6'}$); 69.41, 72.44, 72.87, 74.01 ($C_{1'}$, $C_{3'}$, $C_{4'}$, $C_{5'}$); 107.28 (C_5); 146.29 (C_6); 149.69 (C_2); 166.76 (C_4); 169.50, 169.90, 170.33 (OAc CO's); (triphenysphosphine resonances are omitted). ^{31}P NMR (36.21 MHz, C_6D_6) δ 39.94 (s).

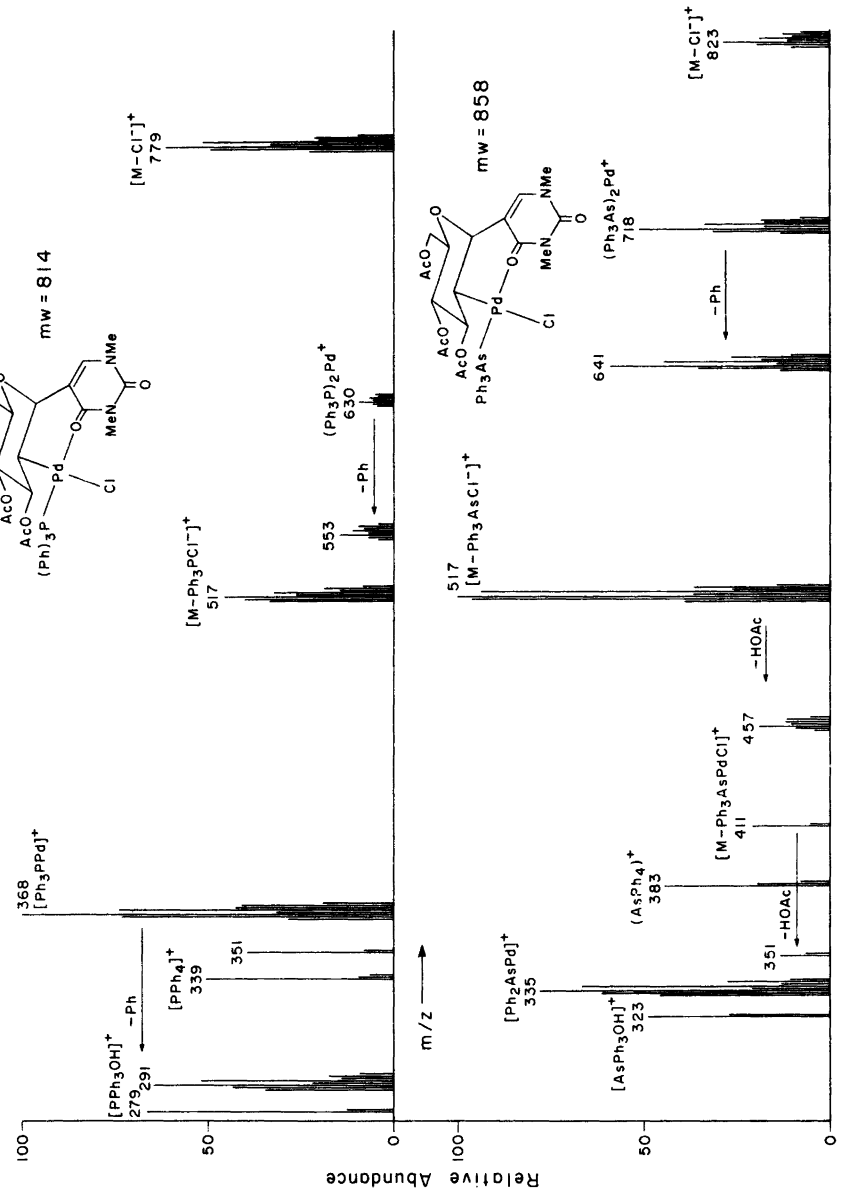


Fig. 1. Fast atom bombardment mass spectra of chloro [1,3-dimethyl-5-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-arabinohexopyranosyl)-2,4-(1*H*,3*H*)-pyrimidinedionnato] (triphenylphosphine) palladium (*1a*, top) and the corresponding triphenylarsine analog (*2a*, bottom).

Anal. calc. for $C_{36}H_{38}ClN_2O_9PPd$: C, 53.0; H, 4.70; N, 3.44; Pd, 13.0. Found: C, 53.1; H, 4.76; N, 3.58; Pd, 12.8. Mol. Weight calc. 816. Found 826 (osmometry in benzene).

*Chloro [1,3-dimethyl-5-(3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-arabinohexopyranosyl)-2,4-(1*H*,3*H*) pyrimidinedionnato] (triphenylarsine)-palladium* (2a). The procedure for the preparation of *1a* was followed except that triphenylarsine was used instead of triphenylphosphine: yield, 43 %. Compound *2a* proved less stable than *1a* and could not be freed completely from excess triphenylarsine. ^{1}H NMR (89.55 MHz, $CDCl_3/C_6D_6$, 1:1): δ 1.58, 1.78, 1.81 (OAc's); 2.32 (dd $J_{2',3'}$=12 Hz, $J_{1',2'}$=5 Hz, $H_{2'}$); 2.92, 3.42 (NMe's); 3.30–3.55 (m, partially obscured, $H_{5'}$); 3.94 (d, J=5 Hz, $H_{6',6''}$); 4.52 (t, J=10 Hz, $H_{4'}$); 4.75–5.05 (m, $H_{1'}$,$H_{3'}$); 7.00 (d, J=1 Hz, H_6); 7.15–7.45, 7.65–7.90 (Ar). ^{13}C NMR (22.51 MHz, $CDCl_3/C_6D_6$, 1:1): δ 20.06, 20.17, 20.78 (OAc Me's); 29.17 (N_3–Me); 30.10 ($C_{2'}$); 37.29 (N_1–Me); 63.02 ($C_{6'}$); 69.58, 72.32, 73.91 ($C_{1'}$, $C_{3'}$, $C_{4'}$, $C_{5'}$); 106. 69 (C_5); 145.86 (C_6); 149.05 (C_2); 167.09 (C_4); 169.26, 169.53, 169.91 (OAc CO's); (triphenylarsine resonances are omitted).

RESULTS

The composition of organopalladium compound *1* was established by elemental analysis[4], molecular weight determination by osmometry, fast atom bombardment mass spectrometry and ^{1}H, ^{13}C and ^{31}P NMR spectrometry. More detailed structural features of *1* were probed by NMR, IR and UV spectroscopies.

Combustion analysis established the elemental composition of *1* as $C_{36}H_{38}ClN_2O_9PPd$ indicative that, formally, palladium bears only three ligands, the *C*-glycosyl moiety, triphenylphosphine and chloride. This result is consistent with (a) a chloride-bridged dimeric structure (*1b*) or (b) a structure in which the *C*-glycosyl moiety provides both a σ and a π bonding site for palladium (*1a*). The dimeric structure *1b* was ruled out by osmometric

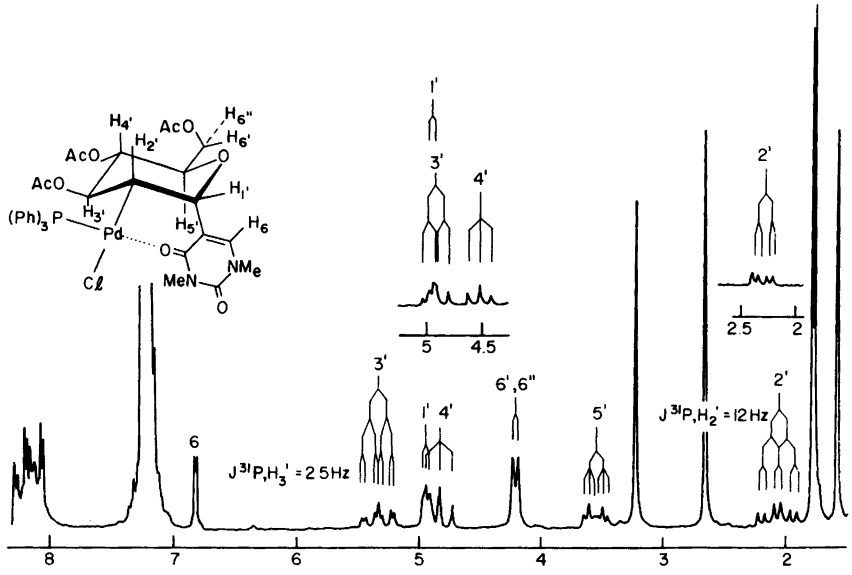


Fig. 2. ^{1}H Nuclear magnetic resonance spectrum of chloro [1,3-dimethyl-5-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-arabinohexopyranosyl)-2,4-(1*H*,3*H*)-pyrimidinedionnato] (triphenylphosphine) palladium (*1a*) in benzene. The inserts show portions of the ^{1}H NMR spectrum of the triphenylarsine analog (*2a*) used to identify ^{31}P, ^{1}H spin-spin interactions. Coupling of the anomeric hydrogen ($H_{1'}$) with H_6 of the pyrimidine moiety is not indicated explicitly.

molecular weight determination using benzene solutions which gave a molecular weight of 826 (calculated for monomer, 816).

Fast atom bombardment (FAB) mass spectra of organopalladium compounds *1a* and *2a* (Figure 1) exhibit ions of highest mass which correspond to $[M-Cl^-]^+$ at *m/z* 779 and 823 respectively confirming the expected nominal compositions of the compounds. Mass spectrometry is not a reliable method for establishing the dominant species (monomer or dimer) of salts in solid or solution states owing to the frequent observation of dimeric and oligomeric cluster ions in their mass spectra.[15] In each mass spectrum, an ion is observed at *m/z* 517 corresponding to palladium plus the *C*-glycosidic residue. Other fragment ions characteristic of the structures of the organopalladium complexes are observed. Noteworthy is the ion at *m/z* 411 in the FAB mass spectrum of *2a* which corresponds to $[MH]^+$ for the product formed upon loss of palladium and β-hydrogen.[4,8] In the spectrum of triphenylarsine compound *2a* (Fig. 1 bottom) ions observed at *m/z* 718 and 641 are not directly related to the complex and may be indicative of decomposition during mass spectrometric analysis.

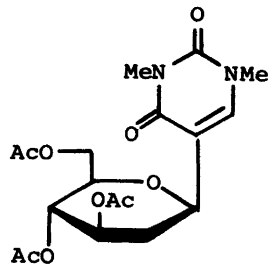
The ^{1}H NMR spectrum of *1a* (Fig. 2) is definitive in establishing the configuration and conformation of the carbohydrate pyranosyl ring. The large coupling constants observed for H−3′, −4′ and −5′ ($J_{3',4'} \simeq J_{4',5'} \simeq 10$ Hz) indicate that these hydrogens occupy axial positions.[16] Similarly, the small magnitude of $J_{1',2'}$ (5 Hz) establishes at least one of these hydrogens as equatorial.[16] Owing to coupling of H−2′ and H−3′ with ^{31}P it was convenient to obtain $J_{1',2'}$ and $J_{2',3'}$ by analysis of the ^{1}H NMR spectrum of the triphenylarsine analog (*2a*) in which $J_{1',2'}$ (5 Hz) and $J_{2',3'}$ (12 Hz) are clearly evident (Fig. 2, inserts). Therefore, $H_{1'}$ is equatorial and the pyrimidinedionyl moiety is axially disposed; $H_{2'}$ is axial and palladium occupies an equatorial position. These data are indicative that the carbohydrate pyranyl ring is in a chair conformation with large substituents at $C_{2'}$ (Pd). $C_{3'}$, $C_{4'}$ (OAc's) and $C_{5'}$ (CH_2OAc) in the more stable equatorial positions; only the pyrimidinyl group at $C_{1'}$ is axial.

Spectroscopic properties of palladium compounds *1a* and *2a* which reveal a π-bonding site for palladium in the pyrimidinedionyl moiety are noted in table 1. Thus, the UV spectrum of palladium compound *1a* exhibits λ_{max} in methanol at 291 nm (Table 1) whereas the pyrimidine chromophore in related, non-metal containing *C*-glycosides, *e.g.* 1,3-dimethyl-2-(3,4,6-tri-*O*-acetyl-2-deoxy-β-D-*arabino*-hexopyranosyl-2,4(1*H*,3*H*)-pyrimidinedione (*3*)[8] exhibits an absorption maximum at 270 nm. Similarly, the IR absorption bands for the pyrimidinedione carbonyl groups of palladium complexes *1a* and *2a* are

Table 1. Spectroscopic properties of palladium complexes indicating bonding between palladium and the pyrimidinyl group.

Compound	UV (MeOH) λ_{max}, nm	IR (KBr-disc) cm^{-1}		^{13}C NMR (C_6D_6),[a] δ					
				N_1-CH_3	C_2	N_3-CH_3	C_4	C_5	C_6
Palladium Complex *1a*	291	1640	1635	38.04	149.69	29.75	166.76	107.28	146.29
Palladium Complex *2a*		1641	1633	37.29	149.05	29.17	167.09	106.69	145.86
2′-deoxy *C*-nucleoside *3*	270[b]	1667	1646	37.18	151.35	27.58	161.70	112.68	139.68

[a] The ^{13}C NMR spectrum of *2a* was recorded in $C_6D_6/CDCl_3$ 1:1. [b] From Ref. 8.



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displaced with respect to those of *3* (Table 1). The ^{13}C NMR resonances for pyrimidine ring carbons are equally indicative of palladium bonding. The ^{13}C resonances for the C_4-carbonyl of palladium complexes *1a* and *2a* are shifted about 5 ppm to lower field as compared with the corresponding resonance for the metal free *C*-nucleoside *3*.[8] The resonances for C_5 of the conjugated double-bond experience shifts of similar magnitude to higher fields, whereas the C_6 resonances are shifted downfield.

All these data, the bathochromic shift of the UV choromophore, the reduced frequency of the carbonyl absorption in the IR and the characteristic ^{13}C NMR resonance shifts (Table 1) indicate a polarization of the pyrimidinedionyl α,β-unsaturated carbonyl system owing to palladium bonding.

The configuration of ligands around palladium is also evident from consideration of the available chemical and spectroscopic data. The structure of the C-nucleoside insures that the $C_{2'}$ σ-bonding site of the carbohydrate and the π-bondind site of the pyrimidine occupy *cis* ligand positions on square planar palladium.[5] That the triphenylphosphine ligand is *cis* to $C_{2'}$ is indicated by the small magnitude of the coupling constant between $C_{2'}$ and ^{31}P; $^2J_{C,P}=2.5$ Hz (see experimental).For comparison, data are reported by Nakazawa, Ozawa and Yamamoto[18] for some *cis* and *trans* $(R_3P)_2PdMe_2$ complexes which exhibit $^2J_{C,P\ (cis)}=10-16$ Hz and $^2J_{C,P\ (trans)}=110$ Hz (see also Refs. 19–22). The ligand arrangement about palladium in complexes *1a* and *2a* accords with studies of Pfeffer *at al.*[23] who have shown that phosphine ligands rarely bond trans to a CH_2 group in palladium compounds.

DISCUSSION

Cyclometalated complexes of transition-metal ions continue to be of intense experimental interest.[24–27] Most metallocycles of transition-metals which have been prepared involve five-membered rings[24–28] and nitrogen donor ligands.[24–29] Six-membered ring metallocycles[28] and metallocycles stabilized by oxygen donor ligands[29] are rare. The available data for the glucopyranosylpalladium complexes establish that the pyrimidinyl group provides a π-bonding site for palladium. Structures *1a* and *2a* in which the C_4 carbonyl group of the pyrimidine ring is π-bonded to palladium, are consistent with the spectroscopic properties of the complexes and are preferred to alternative formulations involving palladium coordination with the pyrimidinyl C_5-C_6 double bond or with a ring nitrogen since these latter structures appear to involve considerable metallocycle ring strain.

The glucopyranosylpalladium metallocyclic system is quite stable in the solid state and is moderately stable at room temperature in solution (acetonitrile, benzene, chloroform) although metallic palladium is formed over a period of hours. This stability is remarkable in view of the presence of a *cis* β-hydrogen,[5–10] the weakness of the oxygen→palladium bond[29] within the metallocycle and the rich decomposition chemistry of the system which includes three separate and selective palladium elimination reactions activated by heating (*syn* β-hydrogen elimination) or upon treatment with acid (*anti* alkoxide elimination with pyran ring rupture) or base (*anti* acetate elimination).[4,8,10]

Presumably, the stability of the complex has its origin in conformational rigidity of the system which establishes a significant barrier to the attainment of the critical alignments of palladium with other pyranosyl ring substituents necessary for the available decomposition modes. Recently, Catellani and Chiusoli[30] have used the presence of such barriers in the rigid norbornylpalladium system to demonstrate some unusual organometallic decomposition reactions and some interesting synthetic applications.

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