the results presented here, stereoselective glycosylations of 2-acylated ribosides which proceed via bridged oxonium ion intermediates exhibit no Lewis acid dependency.

In conclusion, we have presented short, efficient preparations of the oxathiolanyl and dioxolanyl nucleoside analogues, which, as a consequence of their low toxicity, should prove to be important antiretroviral agents. The concept of in situ complexation which we have used here for controlling stereochemistry in the synthesis of these nucleoside analogues should also be applicable to a wide range of other systems and for the preparation of several analogues of **5** and **6**. Further studies involving the preparation and biological activity of these compounds as well as other examples of these types of stereocontrolled glycosylation reactions will be the subject of future reports.

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Supplementary Material Available: Physical data including ^1H and ^{13}C NMR, MS, analytical, and IR data for compounds **5**, **6**, **8**, **9**, **11–13**, and **15** (4 pages). Ordering information is given on any current masthead page.

(14) (i) For N_3: $\beta:\alpha$ = 1:1. Chu, C. K.; Beach, J. W.; Ullas, G. V.; Kosugi, Y. *Tetrahedron Lett.* **1988**, 5349. (ii) For CN: $\beta:\alpha$ = 4:5. Okabe, M.; Sun, R.; Tam, S. T.; Todaro, L. J.; Coffen, D. L. *J. Org. Chem.* **1988**, *53*, 4780. (iii) For SPh: $\beta:\alpha$ = 1:2. Chu, C. K.; Raghavachari, R.; Beach, J. W.; Kosugi, Y.; Ullas, G. V. *Nucleosides Nucleotides* **1989**, *8*, 903.

A Phosphorus Analogue of a Semibridging Aryl Isocyanide Ligand: Synthesis and Structure of (Cl)(PEt$_3$)Pt(μ-C=PR)Pt(PEt$_3$)$_2$(Cl)

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Alkyl and aryl isocyanides (C≡NR) are well-known[1] ligands in transition-metal complexes. They adopt either a terminal (A, Chart I) or bridging (B) mode of coordination to one or two metals, respectively. The phosphorus analogues (C≡PR)[2] of isocyanides are unknown and appear to be unstable[3] relative to the RC≡P isomer.[4] To our knowledge, no complexes containing either terminal (C, Chart I) or bridging (D) C≡PR ligands have been reported. In this paper, we describe the stepwise synthesis of (Cl)(PEt$_3$)Pt(μ-C=PR)Pt(PEt$_3$)$_2$(Cl) (**2**), where R = 2,4,6-tri-*tert*-butylphenyl, and establish that it contains a semibridging C≡PR ligand.

The reaction (eq 1) of Cl_2C=PR[5] (0.359 g, 1.00 mmol) with equimolar Pt(PEt$_3$)$_4$[6] (0.667 g, 1.00 mmol) in 20 mL of benzene at room temperature under nitrogen for 30 min gives the moderately air stable, pale yellow, oxidative-addition product **1**, which is isolated in 85% yield by evaporating the reaction solution to dryness and recrystallizing the residue from hexanes at −78 °C.

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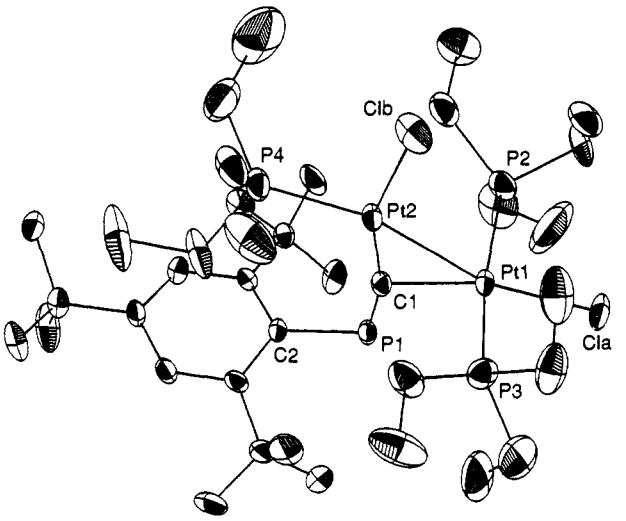


Figure 1. ORTEP drawing of (Cl)(PEt$_3$)Pt(μ-C=PR)Pt(PEt$_3$)$_2$(Cl) (**2**). Selected bond distances (Å) and angles (deg) are Pt(1)–Pt(2) = 2.6751 (5), Pt(1)–C(1) = 2.107 (9), Pt(2)–C(1) = 1.89 (1), P(1)–C(1) = 1.67 (1), P(1)–C(2) = 1.89 (1), C(1)–P(1)–C(2) = 110.7 (5), Pt(1)–C(1)–Pt(2) = 83.8 (4), Pt(1)–C(1)–P(1) = 112.0 (5), and Pt(2)–C(1)–P(1) = 164.1 (6).

Chart I

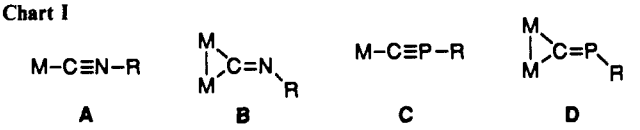
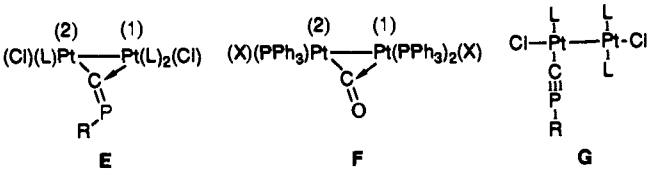
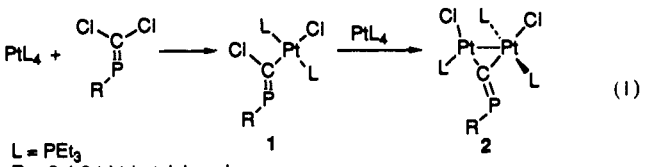


Chart II



Spectroscopic data[7] for **1** are consistent with it having a trans square-planar structure.



(1)

L = PEt_3
R = 2,4,6-tri-t-butylphenyl

When **1** (0.079 g, 0.10 mmol) is reacted (eq 1) with equimolar Pt(PEt$_3$)$_4$ (0.066 g, 0.10 mmol) in 5 mL of hexanes at room temperature under nitrogen for 2 h, red crystals of **2** are isolated[8] in 65% yield by reducing the volume of the reaction solution and cooling it to −30 °C.

An X-ray diffraction study[9] shows **2** (Figure 1) to be a dinuclear

(7) **1**: ^1H NMR (C_6D_6) δ 7.58 (s, 2 H, R), 1.95 (m, 12 H, CH_2 of Et), 1.71 (s, 18 H, CH_3 of R), 1.35 (s, 9 H, CH_3 of R), 1.03 (m, 18 H, CH_3 of Et); $^{31}P\{^1H\}$ NMR (C_6D_6, 85% H_3PO_4 external standard) δ 223.3 (t, $^3J_{PP}$ = 25 Hz, $^2J_{PtP}$ = 658 Hz from ^{195}Pt satellites, C=PR), 15.0 (d, $^3J_{PP}$ = 25 Hz, $^1J_{PtP}$ = 2753 Hz, PEt_3); EIMS (70 eV) *m/e* 790 (M^+), 755 (M^+ − Cl), 733 (M^+ − *t*-Bu), 698 (M^+ − (Cl + *t*-Bu)).

(8) **2**: ^1H NMR (C_6D_6) δ 7.46 (s, 2 H, R), 2.43 (m, 6 H, CH_2), 2.09 (m, 6 H, CH_2), 1.49 (6 H, CH_2), 1.74 (s, 18 H, CH_3 of R), 1.35 (s, 9 H, CH_3 of R), 1.26 (m, 18 H, CH_3 of Et), 0.82 (m, 9 H, CH_3 of Et); $^{31}P\{^1H\}$ NMR (acetone-d_6, 85% H_3PO_4 external standard) δ 151.3 (d, t, $^3J_{P1P2}$ = 23 Hz, $^3J_{P1P4}$ = 35 Hz, $^2J_{Pt,P1}$ = 321 Hz, $^2J_{Pt,P1}$ = 100 Hz), 22.8 (d, $^3J_{P4P1}$ = 35 Hz, $^1J_{Pt2P4}$ = 4814 Hz, $^2J_{Pt1P4}$ = 512 Hz), 19.6 (d, $^3J_{P2P1}$ = 23 Hz, $^1J_{Pt1P2}$ = 2428 Hz, $^2J_{Pt2P2}$ = 45 Hz). Anal. Calcd for $C_{37}H_{74}Cl_2P_4Pt_2$: C, 40.25; H, 6.78. Found: C, 40.36; H, 6.95.

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complex with a bridging μ-C=PR ligand. The atoms C(1), Cl(a), Cl(b), P(4), P(1), C(2), Pt(1), and Pt(2) are all coplanar within 0.134 Å; of the coordinated atoms, only P(2) and P(3) are out of this plane, the Pt(1)-P(2) and Pt(1)-P(3) bond vectors being approximately perpendicular to this plane. The C(1)-P(1) distance (1.67 (1) Å) in the μ-C=PR ligand is the same as the length of the C=P double bond in Ph(H)C=PR, where R = 2,4,6-tri-*tert*-butylphenyl.[10] It is substantially longer than the C≡P triple bond (1.516 (13) Å)[11] in RC≡P (R = 2,4,6-tri-*tert*-butylphenyl) but is shorter than the C(sp^2)—P single bond C(2)—P(1) (1.89 (1) Å) in **2**.

The Pt-C distances to the bridging C=PR from the inequivalent Pt atoms are significantly different; Pt(2)-C(1) (1.89 (1) Å) is 0.22 Å shorter than Pt(1)-C(1) (2.107 (9) Å). Also the Pt-C(1)-P(1) angles are vastly different; the Pt(2)-C(1)-P(1) angle (164.1 (6)°) approaches linearity while Pt(1)-C(1)-P(1) (112.0 (5)°) is sharply bent. Thus, the geometry of the C=PR ligand shows that it is not an analogue of a symmetrically bridging isocyanide as occurs in such compounds as the triangular $Pt_3(\mu\text{-}CNR)_3(CNR)_3$[12] or dinuclear $Cp_2Fe_2(\mu\text{-}CNR)_2(CNR)_2$.[13] The long nonbonding Pt(1)-P(1) distance (3.15 Å) eliminates the possibility that the C=PR ligand is a four-electron donor with π-donation from the C=P bond to Pt(1). Therefore, the most reasonable description of μ-C=PR in this complex is that of a semibridging group, which is strongly coordinated to Pt(2) and interacts more weakly with Pt(1) by accepting at C(1) electron donation from the more electron rich Pt(1) (with two PEt_3 donor ligands) (structure E, Chart II).

Structure E of compound **2** is very similar to that (F) of $(Cl)(PPh_3)Pt(\mu\text{-}CO)Pt(PPh_3)_2(Cl)$[14] and $(Br)(PPh_3)Pt(\mu\text{-}CO)Pt(PPh_3)_2(Br)$,[15] both of which have been described as containing a semibridging CO ligand. As in **2**, the Pt(2)-C-O angle (156 (1)°) is very open and the Pt(2)-C bond distance (1.901 (13) Å) is shorter than that of Pt(1)-C (2.218 (13) Å).[15] In the absence of a semibridging interaction with Pt(1), the C≡PR ligand in **2** would be terminal and have structure G. It is not clear why the C≡PR ligand in **2** and the CO in F prefer the semibridging structure.

In summary, we describe the first example of a metal complex containing a C≡PR ligand. In the reported complex $(Cl)(PEt_3)Pt(\mu\text{-}C{=}PR)Pt(PEt_3)_2Cl$ (**2**), the C≡PR is semibridging, a type of bridging that has not been observed for isocyanide ligands. The synthesis of **2** demonstrates that C≡PR groups can be stabilized in transition-metal complexes.

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Supplementary Material Available: Description of the data collection and structure solution, completely labeled ORTEP drawing of **2**, and tables of crystal data, positional and thermal parameters, complete bond distances and angles, and least-squares planes for **2** (14 pages); listing of calculated and observed structure factors for **2** (20 pages). Ordering information is given on any current masthead page.

(9) Crystallographic data for **2**: mol wt 1103.95; space group $P2_12_12_1$; a = 14.4639 (9) Å, b = 16.152 (2) Å, c = 19.343 (2) Å, V = 4518.8 (9) Å^3, d_{calcd} = 1.62 g/cm^3 for Z = 4 at −50 ± 1 °C, μ = 68.2 cm^{-1} (Mo Kα). Diffraction data were collected at −50 ± 1 °C with an Enraf-Nonius CAD4 automated diffractometer. A total of 8196 reflections were collected. Of the 4227 unique data, 3548 were considered observed, having $F_o^2 > 2.5\ \sigma(F_o^2)$. R = 0.029 and R_w = 0.035. Details of data collection and refinement are given in the supplementary material.

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Molecular Recognition of a Pyrimidine Dimer and Photosensitized Dimer Splitting by a Macrocyclic Bis(diaminopyridine)

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Enzyme–substrate binding is an example of molecular recognition[1] par excellence. Such recognition is a prerequisite for photorepair of pyrimidine dimers in DNA by photolyases, enzymes that bind to dimer-containing DNA in a dark reaction and subsequently split the dimer in a light-dependent step that employs a reduced flavin cofactor.[2] The mode of dimer recognition by photolyases is unknown but is thought to involve contacts of the enzyme, bound across the major groove of DNA, with the cyclobutyl group of the dimer and the phosphates of the DNA backbone.[2a,f,h,i,k] To explore the possible utility of the unique hydrogen-bonding pattern of the dimer's splayed dihydropyrimidine rings in dimer recognition and binding, we have prepared macrocycle **1a**[3] (Figure 1) and found that it has a high affinity for pyrimidine dimer **2** (Chart I). Analogues of the macrocycle **1a** were found to photosensitize pyrimidine dimer splitting.

Binding of **1a** to pyrimidine dimer **2** (1,1′-di-*n*-butylthymine *cis-syn*-photodimer)[4] in $CHCl_3$ resulted in a red shift in UV absorbance (λ_{max} = 291 → 296 nm). Complex formation was also monitored by ^{1}H NMR spectroscopy. A typical titration curve is shown in Figure 1 (upper curve). The largest shift changes occurred in the N-H hydrogens, as a consequence of hydrogen bonding in the complex (e.g., $\Delta\delta$ = 1.23 ppm downfield for **1a** and 3.05 ppm for **2**). Binding of **1a** to **2** was clearly of 1:1 stoichiometry. The association constant[5] was estimated by curve fitting to be on the order of 1.5 ± 0.4 × 10^4 M^{-1}. Repeated titrations gave values on the same order of magnitude. Methyl

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(3) The syntheses of the macrocycles will be presented elsewhere (see supplementary material). For all compounds, high-resolution FAB MS, EI MS, and/or high-resolution (400 or 500 MHz) ^{1}H NMR spectra were consistent with the assigned structures (e.g., high-resolution FAB MS of **1a**: theoretical exact mass for $C_{36}H_{40}N_8O_8S_2 + H^+$ 777.2489, found 777.2485).

(4) Groy, T.; Goodman, M. S.; Rose, S. D., manuscript in preparation.

(5) K_{assoc} may be underestimated due to self-association of **2**. Also, these values may exceed the limit for accurate determination by this method.[11f]

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