Diphenyl arginylvalyl-*N*-methylhydrazinophosphate (1c). In a 250 m*l* Parr low pressure hydrogenation apparatus, diphenyl *N*-carbobenzyloxy-*N*-nitroarginylvalyl-*N*-methylhydrazinophosphate (**8c**) (0.57 g, 0.8 mmol) in methanol (20 m*l*) and 5% palladium on charcoal (0.4 g) were added. Hydrogenation was accomplished under 15 psig of hydrogen pressure. After shaking for 4 hr at room temperature, the mixture was filtered through Celite and the solvent was removed *in vacuo*. The resulted yellow-green oil was chromatographed on silica gel column using ethyl acetate and hexane (2 : 1, v/v) as an eluent, to give a white crystal in 82% yield.

Anal. Calc. for $C_{20}H_{36}N_7O_5P$; C, 49.49; H, 7.42; N, 20.21; O, 16.50; P, 6.39. Found: C, 49.05; H, 7.39; N, 20.65; O, 16.44; P, 6.47. mp. 94℃ (methanol/*n*-hexane); ^{1}H-NMR ($CDCl_3$): δ 1.0 (m, 6H, -CH(CH($C\underline{H}_3$)$_2$), 1.75 (m, 4H, -NHCH$_2$C$\underline{H}_2$C$\underline{H}_2$CH-), 2.1 (m, 1H, -C$\underline{H}$(CH$_3$)$_2$), 2.87 (d, 3H, J=6 Hz, -NC$\underline{H}_3$), 3.2 (m, 3H, -NHC$\underline{H}_2$CH$_2$CH$_2$C$\underline{H}$-), 3.3 (d, 1H, J=5 Hz, -C$\underline{H}$(CH$_3$)$_2$), 7.15 (s, 5H, -OC$_6\underline{H}_5$); IR (KBr): 3500-3200 (Guano group), 1650 (amide), 1250 (P=O), 980 cm^{-1} (P-O-C). (**1a**) mp. 86℃ (ethyl acetate/*n*-hexane); ^{1}H-NMR ($CDCl_3$): δ 3.8 (d, 6H $J_{H\text{-}P}$=7 Hz, -OC$\underline{H}_3$); IR (KBr): 3600-3500 (Guano group), 1680 (amide), 1170 (P=O), 980 cm^{-1} (P-O-C). (**1b**) mp. 89℃ (ethyl acetate/*n*-hexane); ^{1}H-NMR ($CDCl_3$): δ 1.35 (m, 6H, -OCH$_2$C$\underline{H}_3$), 4.3 (m, 4H, -OC$\underline{H}_2$CH$_3$); IR (KBr): 3500-3300 (Guano group), 1660 (amide), 1200 (P=O), 990 cm^{-1} (P-O-C). (**1d**) mp. 185℃ (ethanol/H_2O); IR (KBr): 3550-3300 (Guano group), 1690 (amide), 1150 (P=O), 1000 cm^{-1} (P-O-C).

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Theoretical Studies on the Photochemical Reaction of Psoralen Derivatives

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Psoralens are a family of naturally occurring or synthetic substances which are used in association with UV-A irradiation for treatment of several skin diseases. Psoralen derivatives have been used for many years in the experiments of vitiligo an psoriasis.[1,2] These compounds have also been studied very thoroughly in model systems and with model compounds, and their in *vivo* funtioning is not well understood yet.[3-5]

Various biological targets are likely to be involved in the therapeutic effects observed with such compounds. Their antiproliferative effects are usually related to their ability to undergo photocycloaddition reactions with pyrimidine bases of DNA, and particularly with thymine, leading to the formation of both monofunctional and bifunctional adducts.[6] The molecule which is being much studied at the moment is 3-carbethoxypsoralen (3-CPs).[7] This, unlike 8-MOP, only forms monoadducts and is supposed to be less toxic from the point of view of structure-activity relationship, that is, it is possibly less likely to cause skin cancer.

A mechanistic model for the photochemical reaction in which carcinogenophore contributes to the stabilization of the psoralen derivatives is postulated in our work.

The energy of the triplet state determind from the PM3 calculation appears to be significantly higher in the case of pyridopsoralens (PyPs) than for 3,4-benzopsoralen(3,4-BPs) and 3-CPs, increasing in the order:

4′,5′-BPs<3,4-BPs<3-CPs<PyPs

In the photoreactive psoralen derivatives, the intermolecular π-π interaction is not restricted to the excited states. The electron contour maps in the main molecular planes of excited psoralen derivatives are given in Figure 1.

The pyrone 3,4 and furan 4′,5′-double bonds are necessary

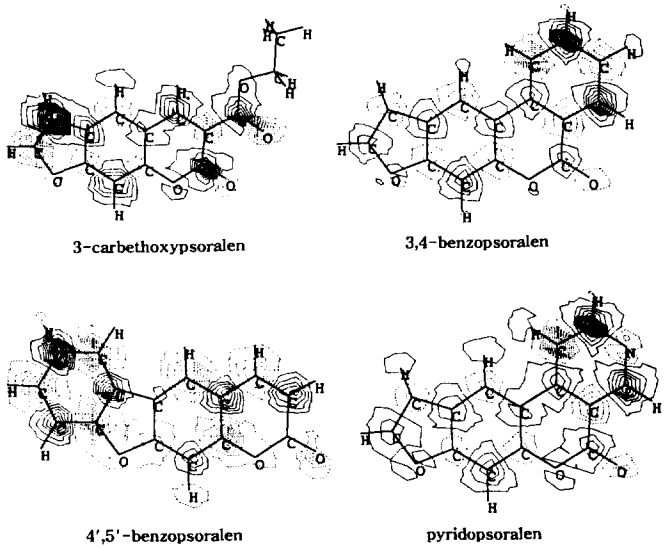

Figure 1. The electron contour maps in the main molecular planes of excited psoralen derivatives.

Table 1. The estimated enrgies and coefficients of the lowest triplet HSOMO and LSOMO of the triplet states by means of PM3-UHF-CI calculation (eV)

Psoralen,	Position	HSOMO	LSOMO
3-CPs	C3	−0.2507	−0.3159
	C4	0.5331	−0.2206
	C5	−0.3737	0.2072
	C4′	0.0936	−0.0430
	C5′	−0.0589	0.1246
	C8	−0.0685	−0.0416
T_1 State Energy		7.06	
3,4-BPs	C3	−0.3626	−0.3149
	C4	0.1754	−0.2274
	C5	−0.3818	0.2450
	C4′	0.0881	−0.0484
	C5′	−0.0646	0.1286
	C8	−0.1548	−0.0798
T_1 State Energy		6.80	
4′,5′-BPs	C3	0.5118	−0.5653
	C4	−0.5253	−0.2435
	C5	0.3565	0.1903
	C4′	−0.0576	0.0091
	C5′	−0.0492	−0.3437
	C8	0.1113	−0.0390
T_1 State Energy		6.77	
PyPs	C3	−0.3593	0.3123
	C4	0.303	0.1558
	C5	=0.3819	−0.1861
	C4′	0.1054	0.0096
	C5′	−0.0568	−0.1898
	C8	−0.1571	0.0478
T_1 State Energy		7.14	

for the photosensitizing activity of psoralens. The 3,4-BPs, 4′,5′-BPs and PyPs without the furan ring in the molecule also intercalates strongly with DNA and photobinds covalently to DNA bases, causing similar biological activities to psoralen derivatives. It is also remarkable that the mobile bond order for C=C in the pyrone moiety experiences a 50% reduction in the excited triplet state.[9] This relationship is further confirmed in Figure 1 which shows that positions, 3 and 4 carry extremely high spin densities. Pyridopsoralens (PyPs) are psoralens with a fused pyridine ring. The fusion of the pyridine ring at the 3,4 double bond of the pyrone moiety leads to compounds which exhibit interesting properties. In order to find out more about the excited state of psoralen derivatives and their possible role in the photosensitization reactions, we have investigated the excited states of four psoralen derivatives; 3-CPs, PyPs, 4′,5′-BPs, 3,4-BPs using PM3-CI-UHF calculations.

Table 1 shows energies of higher singly occupied molecular orbitals (HSOMO) and lower ones (LSOMO) of the triplet states by means of the UHF-CI method. As the photoadditions were sensitized by some triplet sensitizers, they were inferred to go through two step radical paths, and that the first steps were mainly influenced by coefficients and energies of the frontier orbitals, respectively. The frontier electron density can be interpreted as a measure of ability of accepting and donating the electron from an electrophile and to a nucleophile respectively. Since, many cellular components such as DNA and protein are electron rich, it can be considered as nucleophile. Psoralen derivatives are electron poor compared to the cellular components, hence they act as the electrophile when reacting with cellular omponents. The total spin density along the C4′, C5′ shows a minimum at the furan ring in 3-CPs. An interesting comparison is also provided by the corresponding total spin density for the related psoralen derivatives which shows a very similar minimum at the pyrone C3, C4 and furan C4′, C5′.

On the basis of the structure of psoralen derivatives quantum mechanical studies have allowed as to get a better understanding of the photochemical reaction of psoralen derivatives.

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Synthesis and Crystal Structure of $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}CHTol)(\mu\text{-}H)$

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In recent years alkylidyne cluster complexes have received considerable attention due to the potential surface intermediates of the μ_3-alkylidyne fragments in various catalytic reactions.[1] In previous work,[2] we have reported the synthesis and solution dynamics of a tungsten-triosmium *p*-xylylidyne complex, $CpWOs_3(CO)_{11}(\mu_3\text{-CTol})$ (**1**, Cp=η^5-C_5H_5, Tol=*p*-C_6H_4Me). Further investigation of **1** on the reactivity toward dihyrogen has revealed formation of an unexpected hydrido-*oxo*-alkylidene complex, $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-CHTol})(\mu\text{-}H)$ (**2**). Herein we report details of the synthesis and crystal structure of compound **2**.

Experimental Section

General Comments. Solvents were dried prior to use. $CpWOs_3(CO)_{11}(\mu_3\text{-CTol})$ was prepared as described in the literature.[2] All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. The progress of the reactions was monitored by analytical thin-layer chromatography (precoated TLC plates, Silica Gel 560 F-254, E. Merck). Preparative TLC was carried out using glass-backed silica gel plates (20×20 cm) prepared from silica gel G (Type 60, E. Merck). Infrared spectra were obtained on a Nicolet 5-MX FT-IR spectrophotometer. ^{1}H-NMR (300 MHz) spectra were recorded on a Bruker AM-300 spectrometer. Mass spectra were recorded by the staff of the Analytical Laboratory at the Lucky Ltd. using JEOL DX-300 mass spectrometer. All m/z values are referenced to ^{184}W and ^{192}Os.

Reaction of 1 with Dihydrogen. Compound **1** (20 mg, 0.016 mmol) was dissolved in toluene (25 mL) in a 250 mL glass pressure bottle. The resulting solution was degassed by the freeze-pump-thaw cycle and the bottle was charged with dihydrogen gas to a pressure of 50 psig. The resulting solution was heated at 110℃ for 2.5 h. Evaporation of the solvent *in vacuo* and purification by preparative TLC (petroleum ether : dichloromethane = 1 : 2) gave $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-CHTol})(\mu\text{-}H)$ (**2**, 0.0097 mmol, 60%, R_f=0.6) as an orange solid: ^{1}H-NMR ($CDCl_3$, 25℃) δ 7.06-6.44 (AB pattern, 4H), 5.94 (s, 5H), 5.52 (d, J=1.7 Hz, 1H), 2.41 (s, 3H), −18.05 (d, J=1.7 Hz, 1H); IR (C_6H_{12}) ν(CO) 2090 (s), 2064 (vs), 2026 (vs), 2014 (s), 2006 (m), 1990 (w), 1954 (w), 1937 (m), cm^{-1}; MS (70 eV) m/z 1198 (M^+).

Table 1. Crystal Data for **2**

formula	$C_{22}H_{14}O_{10}WOs_3$
f_w	1192.79
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	10.837(2)
b, Å	26.073(2)
c, Å	9.232(2)
β, deg	103.33(2)
V, Å^3	2538(1)
Z	4
ρ(calcd), gcm^{-3}	3.12
temp. ℃	21
λ(MoKα), Å	0.71069

Crystal Structure of 2. Crystals of compound **2** suitable for an X-ray analysis were obtained by slow recrystallization from a mixture of petroleum ether and dichloromethane at −10℃. Space group and approximate cell dimensions of this crystal were determined by preliminary experiment using Weissenberg and precession photography.[3] The diffraction symmetry ($2/m$, C_{2h}) and systematic absence (*h* 0 *l for* $h+l=2n+1$ and 0*k*0 for $k=2n+1$) uniquely defined the centrosymmetric monoclinic space group $P2_1/n$. An opaque dark red crystal of approximate orthogonal dimensions of 0.2×0.4×0.2 mm was mounted and aligned on a CAD-4 diffractometer. Details of the relevant crystallographic data are given in Table 1. The accurate cell parameters were refined from setting angles of 25 reflections with $10°<\theta<14°$, and intensity data for 3822 independent reflections in range $0\leq h\leq 11$, $0\leq k\leq 28$, $-10\leq l\leq 10$ were collected using graphite-monochromated Mo K_α radiation and ω/2θ scan mode, ω-scan width=$(0.8+0.35\tan\theta)°$, $\theta_{max}=25°$. All data were converted to E_o values following correction for L-P and absorption factors. The four heavy atoms were located by using direct method (SDP)[4] and all non-hydrogen atoms were found on subsequent difference Fourier maps. The structure was refined by full-matrix least squares program with SHELX[5] and function minimized was $\Sigma\omega(|F_o|-|F_c|)^2$, where $\omega=1.0/(\sigma^2(F_o)+0.001834\,F_o^2)$. Independent reflections of 2790 [$F_o>3\sigma(F_o)$] were used for the structure refinement and number of parameters refined was 338. A final difference Fourier synthesis showed a number of small peaks in the vicinity of the heavy atoms. A bridging hydride ligand could not be located with any certainty. However, thirteen hydrogen atoms attached to the C(1), Cp and Tol moieties were calculated from the known stereochemistry by adopting the C-H distances of 1.08 Å and refined with isotropic thermal parameters. Neutral atomic scattering factors were used with W and Os corrected for anomalous dispersion.[6] Final reliability factors were R=