

## d-d Band Excitation of the Diorganonickel(II) Complexes $trans-[Ni\{2,6-(MeO)_2C_6H_3\}_2L_2]$ (L = $PMe_3$ or $PMe_2Ph$ ) and Their Analogues causing Reversible Phosphine Dissociation and/or Organic Group Rotation about the Ni-C Bond

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The title photo-reactions were observed to give stationary state mixtures, which are different from those resulting from thermal equilibrations.

Square-planar diorganonickel(II) complexes,  $trans-[NiR_2L_2]$ , are commonly yellow to orange owing to the presence of the so-called 'd-d band' in their electronic spectrum.<sup>1</sup> The complexes (**1a**), (**1b**), (**2a**), (**2b**), (**3a**), and *syn*- and *anti*-(**3b**) also exhibit such a band<sup>†</sup> in the 360–400 nm region as a shoulder on very intense bands in the u.v. region tailing towards the visible region. Since the d-d excitation would transfer an electron in a non-bonding d orbital to the antibonding  $d_{x^2-y^2}$  orbital, we thought that it would weaken the Ni-R and/or the Ni-L bonds. We have now studied the photoreaction of complexes (**1**)–(**3**) in order to investigate the excitation effects on their Ni-L and Ni-R bonds.

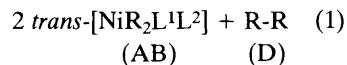
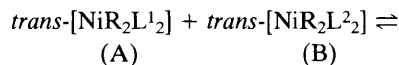
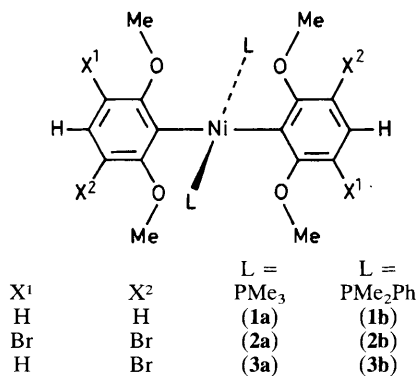
<sup>†</sup> (**1a**), 360; (**1b**), 375; (**2a**), 374; (**2b**), 397; *anti*-(**3b**), 385; *syn*-(**3b**), 384 nm;  $\epsilon$  300–750 (in  $C_6H_6$  or  $CH_2Cl_2$ ).

The reactions were monitored by the <sup>1</sup>H n.m.r. spectra of 0.03–0.05 M degassed solutions, as in our previous work on thermal reactions.<sup>2,3</sup> Complexes (**1a**) and (**1b**) are stable in benzene at 35 °C, and little change was observed in their <sup>1</sup>H n.m.r. spectra after 4 h irradiation by a 500 W Xe lamp. When a 1 : 1 mixture of (**1a**) and (**1b**) in benzene was irradiated for 1–8 h, the spectrum showed the formation of the mixed ligand complex (AB),  $trans-NiR_2(PMe_3)(PMe_2Ph)$  (**1ab**) [equation (1)] together with a small amount of the decomposition product  $R_2$  (Table 1). The proportion of (**1ab**) increased with irradiation time, although on prolonged irradiation the solution became turbid owing to decomposition. In the dark at 35 °C, much less (**1ab**) was formed. The use of a u.v. filter to remove light below 350 nm did not change the yield of (**1ab**) appreciably.

**Table 1.** Photo-induced intermolecular tertiary phosphine exchange<sup>a</sup> for complexes (1) and (2) [equation (1)].

Complex		Solvent	Time/h	(A):(B):(AB):(D)	
(A)	(B)			Irradiated	[Dark (24 h)]
(1a)	(1b)	C <sub>6</sub> H <sub>6</sub>	1	45:45:10:0	[47:49:4:0]
			8	26:28:41:5	
(2a)	(2b)	CH <sub>2</sub> Cl <sub>2</sub>	1	39:38:20:3	[46:43:11:0]
			11	17:16:62:5	

<sup>a</sup> Degassed solutions of (A) and (B) (0.05 M each) were irradiated by a 500 W Xe lamp at 35 °C in n.m.r. tubes.



For complexes (2a) and (2b), the fifth and the sixth co-ordination sites of nickel are completely obstructed by the four methoxy groups because of the influence of the *meta*-bromo substituents, as confirmed by an X-ray crystal structure determination,<sup>4</sup> and by the very low reactivity of these complexes towards carbon monoxide.<sup>2</sup> Photo-induced ligand exchange was still observed between these complexes, however, suggesting a mechanism involving three-coordinate intermediates.

A benzene solution containing (1a) and free PMe<sub>2</sub>Ph (1.5 equiv.) gave on heating at 81 °C a thermal equilibrium mixture

of (1a), (1ab), and (1b) (78:22:1). Interestingly, on 4 h irradiation of this equilibrated mixture at 35 °C, the ratio changed to 56:41:3. On heating this solution, the thermal equilibrium was restored.

Complexes (3a) and (3b) exist in both *anti* and *syn* forms owing to the lack of free rotation of the organic group around the Ni-C bonds, and both isomers have been separated in pure form for (3b).<sup>3</sup> When a benzene solution of *anti*-(3b) was irradiated at 35 °C, it partially isomerized to *syn*-(3b). Analogous isomerization was observed for *syn*-(3b). Both isomerizations resulted in a stationary state with an *anti* to *syn* ratio of 68:32 after 8 h irradiation, a different ratio from the thermal equilibration (*anti*:*syn* 50:50).<sup>3</sup> In the dark at 35 °C, neither isomer isomerized in solution for at least 8 h. Analogous isomerization differences between the photo and thermal reactions were observed for (3a) to give a photo-stationary state with an *anti*:*syn* ratio of 64:36, compared with the thermally equilibrated ratio of 55:45.

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## References

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