

The Effect of Metal–Metal Bonding on the Regiospecificity of Nucleophilic Addition to Carbonyl Ligands in Complexes of the Type $[(OC)_4M(\mu-PPh_2)_2Pt(PR_3)]$ and Analogues

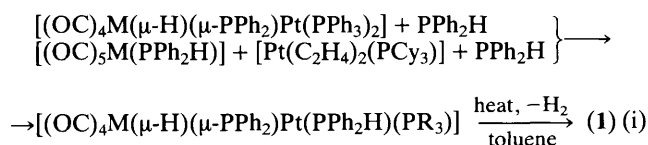
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Regiospecific nucleophilic addition of PhLi to the equatorial CO of $[(OC)_4M(\mu-PPh_2)_2M'L_x]$ is considered to be a direct consequence of $M \rightarrow M'$ bonding rather than due to steric effects, and contrasts with the lack of reactivity of PhLi with $cis-[(OC)_4M(PR_3)_2]$ and the general observation that in octahedral systems a CO *trans* to CO (as opposed to PR_3) is more susceptible to nucleophilic addition.

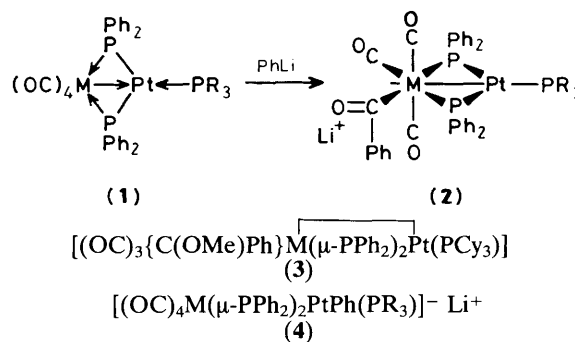
Nucleophilic addition to a co-ordinated CO ligand represents an important reaction pathway in transition metal carbonyl chemistry. For octahedral Group VI metal carbonyls of the type $[(R_3P)M(CO)_5]$, the equatorial carbonyl groups (CO *trans* to CO) are the more susceptible to nucleophilic addition.^{1,2} Thus reaction with RLi gives $cis-[(R_3P)M(RCO-Li)(CO)_4]$. Increasing phosphine substitution reduces the susceptibility of the CO ligand to nucleophilic addition and the complexes $cis-[(R_3P)_2M(CO)_4]$ do not react with RLi, although one would predict that the axial CO groups (*trans* to CO) of $cis-[(R_3P)_2M(CO)_4]$ would be the preferred sites for nucleophilic addition.² In contrast to $cis-[(R_3P)_2M(CO)_4]$ there are now several reports of bimetallic systems of the type $[(OC)_4M(\mu-PPh_2)_2M'L_x]$, which contain M–M' bonding, in which (i) the CO ligands are susceptible to nucleophilic addition or (ii) it is a CO ligand *trans* to a phosphido group that is more susceptible to nucleophilic addition, rather than the axial CO groups (*trans* to CO).^{3,4} Whilst it has been previously suggested that the regiospecificity of RLi addition is a consequence of steric effects,⁵ we here present evidence that the increased reactivity and unusual regiospecificity in $[(OC)_4M(\mu-PPh_2)_2M'L_x]/RLi$ systems are an effect of direct M–M' bonding.

The complex $[(OC)_4M(\mu-PPh_2)_2Pt(PR_3)]$ (1) (M = Mo or W; $PR_3 = PCy_3$), [see equation (i) for preparation] reacts with



a molar equivalent of PhLi to give $[(OC)_3(PhCOLi)-M(\mu-PPh_2)_2Pt(PCy_3)]$ (2) quantitatively.[†] Complexes (2), isolated as extremely air/moisture-sensitive powders, were characterized spectroscopically[‡] and have i.r. (ν_{CO} region) and $^{31}P\{^1H\}$ n.m.r. data very similar to those reported for $[(OC)_3(PhCOLi)W(\mu-PPh_2)_2Ir(H)(CO)(PPh_3)]$.³

Addition of $(Me_3O)BF_4$ to (2) gives the carbene complexes $[(OC)_3\{C(OMe)Ph\}M(\mu-PPh_2)_2Pt(PCy_3)]$ (3) (carbene *trans* to $\mu-PPh_2$), structurally similar to $[(OC)_3\{C(OMe)Ph\}W(\mu-PPh_2)_2Ir(H)(CO)PPh_3]$,³ and $[(OC)_3\{C(OMe)-$



[†] The complex $[(OC)_4W(\mu-PPh_2)_2Pt(PPh_3)]$ has been previously reported but its reactivity with RLi reagents was not commented on.⁶

[‡] E.g. for (2) (M = W; $PR_3 = PCy_3$) δ (P_a) 158, δ (P_b) 141, δ (P_c) 37 p.p.m.; J ($^{195}Pt-^{31}P$) 2835 (P_a), 2430 (P_b), and 4864 (P_c); J ($^{183}W-^{31}P$) 199 and 189 (P_a, P_b); J ($^{31}P-^{31}P$) 198 (P_a-P_b), 61 (P_a-P_c), and 11 (P_b-P_c) Hz.

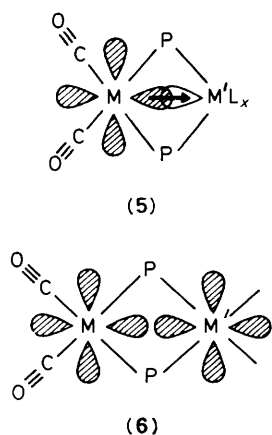
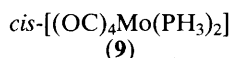
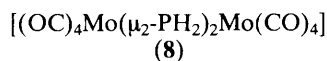
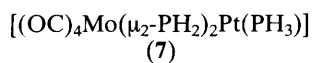


Figure 1

Ph}W(μ -PPh₂)₂Re(CO)₃Me].⁴ Complexes (1) (M = Mo or W; PR₃ = PPh₃ or PEt₃) react with PhLi in THF to give mixtures of [(OC)₃(PhCO)M(μ -PPh₂)₂Pt(PR₃)] (2) and [(OC)₄M(μ -PPh₂)₂PtPh(PR₃)]-Li⁺ (4) (no M-Pt bond). The tendency for nucleophilic addition at Pt, rather than at CO, decreases with increasing 'size' of the PR₃ ligand (PEt₃ > PPh₃ >> PCy₃). The observed regioselectivity of RLi addition to an equatorial CO of the complexes (1), [(OC)₄-W(μ -PPh₂)₂Ir(H)(CO)(PPh₃)₂],³ [(OC)₄W(μ -PPh₂)₂Re(CO)₃-Me],⁴ and [(OC)₄M(μ -PPh₂)₂M(CO)₄] (M = Mo or W)⁵ contrasts with the behaviour of [(OC)₄W(μ -PPh₂)₂ZrCp₂]⁷ and [(CO)₄Mo(μ -PEt₂)HfCp₂]⁸ (no M-M' bonds, or very weak ones), which do not react with RLi. A qualitative rationale for these observations can be obtained from consideration of the simple bonding representations (5) and (6) (Figure 1) for systems with and without a metal-metal bond. If one assumes that a filled d_{xy} orbital of M is involved to a significant extent in a direct M → M' dative bond in (5) then the net result will be a decrease in d_{xy} → π*CO bonding to the equatorial CO (*trans* to P_μ) and an increased susceptibility of these CO groups to nucleophilic addition at C *vis-à-vis* the equatorial CO groups of (6). Extended Hückel molecular orbital calculations and the fragment orbital formalism^{9,10} have been utilized to study the three model complexes (7)–(9). §



According to the calculations, it appears that nucleophilic attack at the carbon of the carbonyl ligand may be considered to be of frontier orbital type and charge-controlled. Table 1 contains the electronic distribution of the carbon atoms of the carbonyl ligands of the LUMO of each of the three complexes. The regioselectivity of RLi addition correlates well with the relative magnitude of the electron density of both available

Table 1. Net charge for the axial and equatorial carbonyl carbon atoms for the metallic fragments and complete molecules. The electronic distributions at the carbon atoms in the LUMO of compounds (7), (8), and (9) are in parentheses.

Fragment/Molecule	Axial CO	Equatorial CO
(OC) ₄ Mo : Pt(PH ₃)	0.70	0.68
[(OC) ₄ Mo(μ -PH ₂) ₂ Pt(PH ₃)] (7)	0.71 (0.06)	0.76 (0.13)
(OC) ₄ Mo : Mo(CO) ₄	0.71	0.68
[(OC) ₄ Mo(μ -PH ₂) ₂ Mo(CO) ₄] (8)	0.72 (0.03)	0.78 (0.14)
(OC) ₄ Mo :	0.73	0.66
[(OC) ₄ Mo(PH ₃) ₂] (9)	0.73 (0.75)	0.67 (0.02)

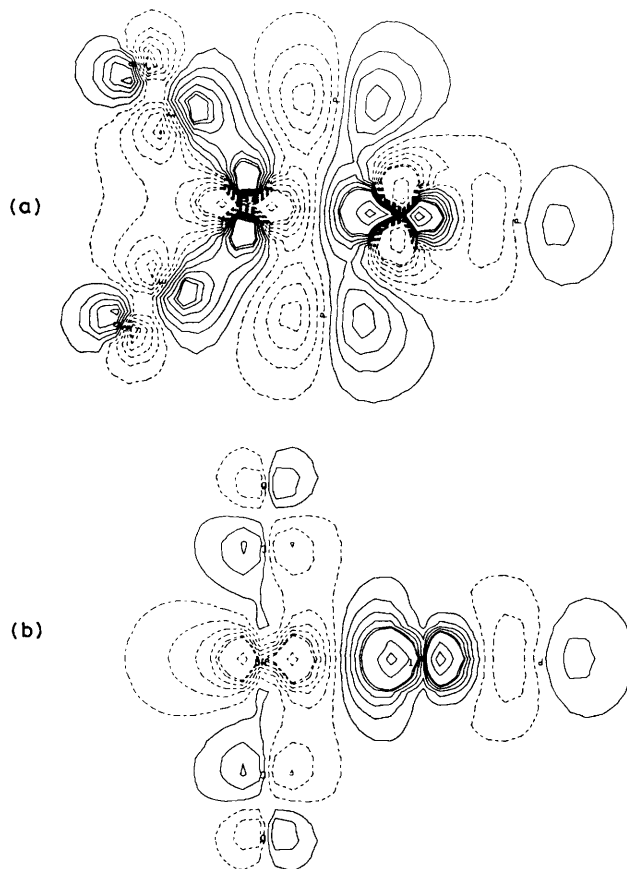


Figure 2. Electron density plot for the LUMO of [(OC)₄Mo(μ -PH₂)₂Pt(PH₃)] (7): (a) xy plane (equatorial CO); (b) xz plane (axial CO).

sites in the LUMO. Model compounds (7) and (8), containing phosphido bridges, have a higher electron density in the equatorial (*i.e.* *trans* to phosphorus) CO groups than in the axial CO groups (see Figure 2) and *vice versa* for the *cis*-phosphine complex (9). The regioselectivity of the nucleophilic attack also correlates with the electropositive character at the carbon atom of the carbonyl ligand. Table 1 shows the net charge for both axial and equatorial carbon of the CO groups for the complete molecules, and, to emphasize the effect of the phosphido bridges, the net charges are also presented for the metallic fragments without the bridging ligands. In the monomer (9), the axial carbon atoms are far more electropositive than those *trans* to the PH₃ ligands. The situation is reversed when phosphido bridges are *trans* to the CO groups. The effect of adding the phosphido bridges to the metallic fragments is an increase in the electropositivity of the equatorial carbon atoms of about 12–15%, whilst that of the

§ Interatomic distances based on X-ray structural determinations of [(OC)₄Mo(μ -PPh₂)₂Pt(PEt₃)]¹¹ [(OC)₄Mo(μ -PEt₂)₂Mo(CO)₄]¹² and [(OC)₄Mo(PEt₃)₂]¹³ with idealised C_{2v} (7), D_{2h} (8), and C_{2v} (9) geometries. The d-orbitals on the phosphorus atoms were not included in the calculations.¹⁴

the carbon atoms of the axial CO groups remains unchanged, consistent with the simple qualitative assessment given in Figure 1. These results provide an unusually clear illustration of the way in which 'co-operativity effects' (namely the perturbations of the chemistry at one metal centre by a second metal in close proximity) can occur.

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