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Photoelectron Spectra of Complexes [W(CO)$_5$(PMe$_n$Ph$_{3-n}$)]: Triphenylphosphine is a Stronger Base than Trimethylphosphine

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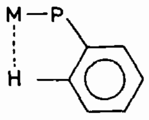
There has been much discussion about the relative basicities of the ligands PMe$_n$Ph$_{3-n}$ [1–3]. Although PMe$_3$ is the strongest Bronsted base in aqueous solution, PPh$_3$ is the strongest Bronsted base in the gas phase [1]. Arguments have been made that PPh$_3$ is the strongest Lewis base [2, 4], but most workers still regard PMe$_3$ as the strongest Lewis base in this series of phosphines [3]. For the phosphine complexes of linear or square planar gold(I), gold(III) or platinum(II) complexes, the ionization energies of non-bonding 5*d*-orbitals follow the sequence [4] L = PPh$_3$ < PMePh$_2$ < PMe$_2$Ph < PMe$_3$, and this trend was interpreted either in terms of the Lewis basicity sequence PPh$_3$ > PMePh$_2$ > PMe$_2$Ph > PMe$_3$, or by a special bonding interaction of the phenyl phosphines involving an *ortho*-hydrogen atom of the ligand and the metal centre, 1 [3, 4].



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In order to distinguish between these interpretations, photoelectron spectra have been recorded for the series of complexes [W(CO)$_5$(PMe$_n$Ph$_{3-n}$)], which are co-ordinatively saturated and hence cannot undergo the *ortho*-interaction, 1.

The He I photoelectron spectra of the complexes were recorded as described previously [5], and assignments were straightforward by comparison with spectra of similar complexes [6]. Data are summarized in Table I and the following trends are significant:

1. There is a dramatic increase in the energy of stabilization Δ, of the phosphorus lone pair on co-ordination along the series PMe$_3$ < PMe$_2$Ph < PMePh$_2$ < PPh$_3$ (Table II), as expected if PPh$_3$ is the strongest σ-donor [4]. The effect is so great that a conjugative interaction with the phenyl π-system is considered probable. This proposed interaction is shown as a qualitative MO diagram in Fig. 1 where, for the purpose of illustration only, it is assumed that the energies of the phosphorus lone pair orbital, n(P), for the free phosphines and the σ(W–P) orbital for the co-ordinated phosphines would be the same for PMe$_3$ and PPh$_3$ in the absence of conjugation. In the free ligand n(P) is higher in energy than the phenyl π-level and so is *destabilized* by conjugation [7] whereas, in the complex, σ(W–P) is lower in energy than the phenyl π-level and so is *stabilized* by conju-

TABLE II. Stabilization Energies, Δ = *IE*[σ(W–P)] – *IE*[n(P)], eV, for Ligands L.

L	*IE*[n(P)]	*IE*[σ(W–P)]	Δ
PMe$_3$	8.62	10.08	1.46
PMe$_2$Ph	8.32	10.28	1.96
PMePh$_2$	8.28	10.33	2.05
PPh$_3$	7.80	10.44	2.64

TABLE I. Vertical Ionization Energies (eV) from the He I Photoelectron Spectra of [W(CO)$_5$(PMe$_n$Ph$_{3-n}$)].

Assignment	W(CO)$_5$(PMe$_3$)	W(CO)$_5$(PMe$_2$Ph)	W(CO)$_5$(PMePh$_2$)	W(CO)$_5$PPh$_3$
W(5*d*)	7.46 7.64 7.90	7.34 7.56 7.81	7.23 7.42 7.71	7.20 7.41 7.67
Ph(π)	– –	– 9.49	8.83 9.42	8.75 9.37
W–P	10.08	10.28	10.33	10.44
5σ + 1π(C–O)	11.85 12.56 14.01	11.68 12.44 14.05	11.27 12.17 14.26	11.14 12.16 14.20
4π(C–O) + Background	17.19	17.51	16.93	15.51

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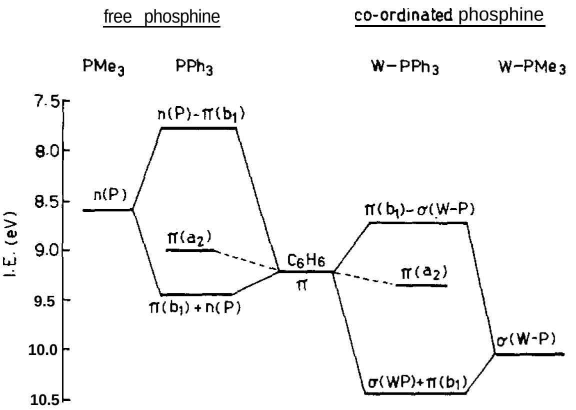

Fig. 1. Qualitative MO diagram.

gation. We suggest that it is the combination of σ- and n-bonding effects which leads to a much greater value of A for PPh_3 compared to PMe_3 and that this effect will be important and general for tertiary phosphine complexes.

2. The ionization energies of the tungsten *5d*-orbitals follow the series $PMe_3 > PMe_2Ph > PMePh_2 > PPh_3$, again indicating that PPh_3 is the strongest donor [4]*. The magnitudes of the splitting of the tungsten t_{2g} orbitals, arising from spin-orbit coupling and n-bonding effects [6], are almost identical for the series of complexes, showing that the phosphine ligands have very similar n-bonding abilities [6].

Since there can be no *ortho*-interaction in these complexes, these results give the most powerful evidence yet found for the u-donor series $PPh_3 > PMePh_2 > PMe_2Ph > PMe_3$†. We emphasize, however, that differences in steric effects between PMe_3 and PPh_3 are probably of great significance in determining the reactivity of complexes with these ligands.

Acknowledgement

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*Differential electron relaxation on ionization may contribute towards this trend, but such effects are most unlikely to reverse the trend in σ-donor series.

†The greater σ-donor power of PPh_3 over PMe_3, is also indicated by a recent ^{13}C NMR study of $[W(CO)_5L]$.^1J-($^{183}W^{13}C$) for the CO ligand ***trans*** to L = 145 Hz when L = PMe_3 and 140 Hz when L = PPh_3 [8].