Synthesis and Characterization of Mono- and Di-cyclometallated Compounds of Symmetric and Asymmetric Azines with Palladium(II) and Manganese(I). *X*-Ray Crystal Structure of $[Mn(C_6H_4CH{=}N{-}N{=}CHPh)(CO)_4]$ †

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The reaction of symmetric benzalazines, $(p\text{-}RC_6H_4CH{=}N{-})_2$ (R = NO_2, Cl, H, or NMe_2), with $Pd(O_2CMe)_2$ gives mono- or di-metallated compounds, $[\{Pd(p\text{-}RC_6H_3CH{=}N{-}N{=}CHC_6H_4R\text{-}p)(O_2CMe)\}_2]$ (R = Cl or H) or $[\{Pd(p\text{-}RC_6H_3CH{=}N{-})(O_2CMe)\}_n]$ (R = NO_2, Cl, H, or NMe_2), depending on the amounts of reactants used. The analogous reactions with $[MnMe(CO)_5]$ lead also to the formation of mono- or di-metallated compounds, $[Mn(p\text{-}RC_6H_3CH{=}N{-}N{=}CHC_6H_4R\text{-}p)(CO)_4]$ or $[\{Mn(p\text{-}RC_6H_3CH{=}N{-})(CO)_4\}_2]$ (R = H or NMe_2). Equimolar amounts of asymmetric benzalazines, $p\text{-}R^1C_6H_4CH{=}N{-}N{=}CHC_6H_4R^2\text{-}p$ (R^1 = H, R^2 = NO_2; R^1 = H, R^2 = Cl; R^1 = NMe_2, R^2 = NO_2), and $Pd(O_2CMe)_2$ yield monometallated compounds in which the electron-rich ring has been preferably metallated. With $PdCl_2$, only the dimetallated compound $[\{ClPd(p\text{-}ClC_6H_3CH{=}N{-}N{=}CHC_6H_4)PdCl\}_n]$ is obtained. No cyclomanganated compound is obtained by reaction of $p\text{-}O_2NC_6H_4CH{=}N{-}N{=}CHPh$ and $[MnMe(CO)_5]$. The mixed-metal cyclometallated compounds $[\{ClPd(p\text{-}RC_6H_3CH{=}N{-}N{=}CHC_6H_3R\text{-}p)PtCl\}_n]$ (R = H or Cl) are obtained from monocyclopalladated $[\{Pd(p\text{-}RC_6H_3CH{=}N{-}N{=}CHC_6H_4R\text{-}p)(O_2CMe)\}_2]$ and $PtCl_4^{2-}$. These comparative studies of palladation and manganation show that the mechanisms proposed for the metallation of azobenzenes are not entirely applicable to benzalazines. The polymeric and dimeric cyclopalladated compounds were converted into mononuclear species by action of PEt_3 for an easy characterization. Structures for the new compounds are assigned on the basis of i.r. and n.m.r. (^1H, ^{13}C, ^{31}P) spectra. The molecular structure of $[Mn(C_6H_4CH{=}N{-}N{=}CHPh)(CO)_4]$ has been determined by a single-crystal *X*-ray structural analysis. The crystals are monoclinic, space group $C2/c$, with $a = 20.591(3)$, $b = 20.517(3)$, $c = 12.466(2)$ Å, $\beta = 140.78(2)^\circ$, $Z = 8$; $R = 0.059$ for 1 896 observed reflections. The manganese atom is co-ordinated in a distorted octahedral configuration, to four carbonyl groups and to the chelating ligand.

The cyclometallation of N-donor ligands has been the subject of a large number of studies in the past few years.[1] However, less attention has been paid to ligands with two nitrogen atoms and capable of undergoing double metallation. Azobenzenes are readily cyclometallated by Mn,[2] Fe,[2] Re,[2] Ru,[2] Ni,[3] Pd,[4] and Pt,[4] but dicyclometallated compounds have been described only with Mn[5] and Ni.[6] Trofimenko[7] reported the formation of dipalladiobenzenes by reaction of *N,N,N',N'*-tetra-alkylxylenediamines with equimolar amounts of $PdCl_4^{2-}$.

Asymmetric ligands are particularly suitable for studying the influence of steric and electronic effects of substituents on reaction mechanisms. Thus, the reaction of asymmetric fluoro-substituted azobenzenes with $[MnMe(CO)_5]$ and $PdCl_2$ has permitted the proposal that manganation and palladation reactions can be described as nucleophilic and electrophilic, respectively.[8] Recently, Klaus and Rys[9] described the cyclopalladation of asymmetric 1-phenylazonaphthalenes and compared the different reactivities of the phenyl and naphthyl rings. They proposed that the regioselectivity of the metallation depends on the facility of the ring to experience electrophilic attacks and on the relative basicity of the nitrogen atoms.

Benzalazines are able to undergo double metallation, but only the monometallated compounds $[Mn(C_6H_4CH{=}N{-}N{=}CHPh)(CO)_4]$[10] and $[\{Pd(C_6H_4CH{=}N{-}N{=}CHPh)(O_2CMe)\}_2]$,[11] obtained by reaction of benzaldehyde azine with $[MnMe(CO)_5]$ and $Pd(O_2CMe)_2$, respectively, have been described.

Following our studies of dimetallated azine compounds,[12–14] we now report here the obtention of mono- and di-cyclometallated compounds of symmetric and asymmetric benzalazines with Pd^{II} and Mn^I. It has also been possible to obtain binuclear mixed-metal complexes of the symmetric azines with palladium and platinum. A preliminary note on the mixed-metal complexes has been published.[15] The electronic effects of the benzalazine substituents on the reaction mechanism are also discussed.

Results and Discussion

The action of $Pd(O_2CMe)_2$ on the azines $(p\text{-}RC_6H_4CH{=}N{-})_2$ [R = NO_2 (**1a**), Cl (**1b**), H (**1c**), or NMe_2 (**1d**)] in anhydrous acetic acid under reflux and with a Pd: azine ratio of 2:1 leads

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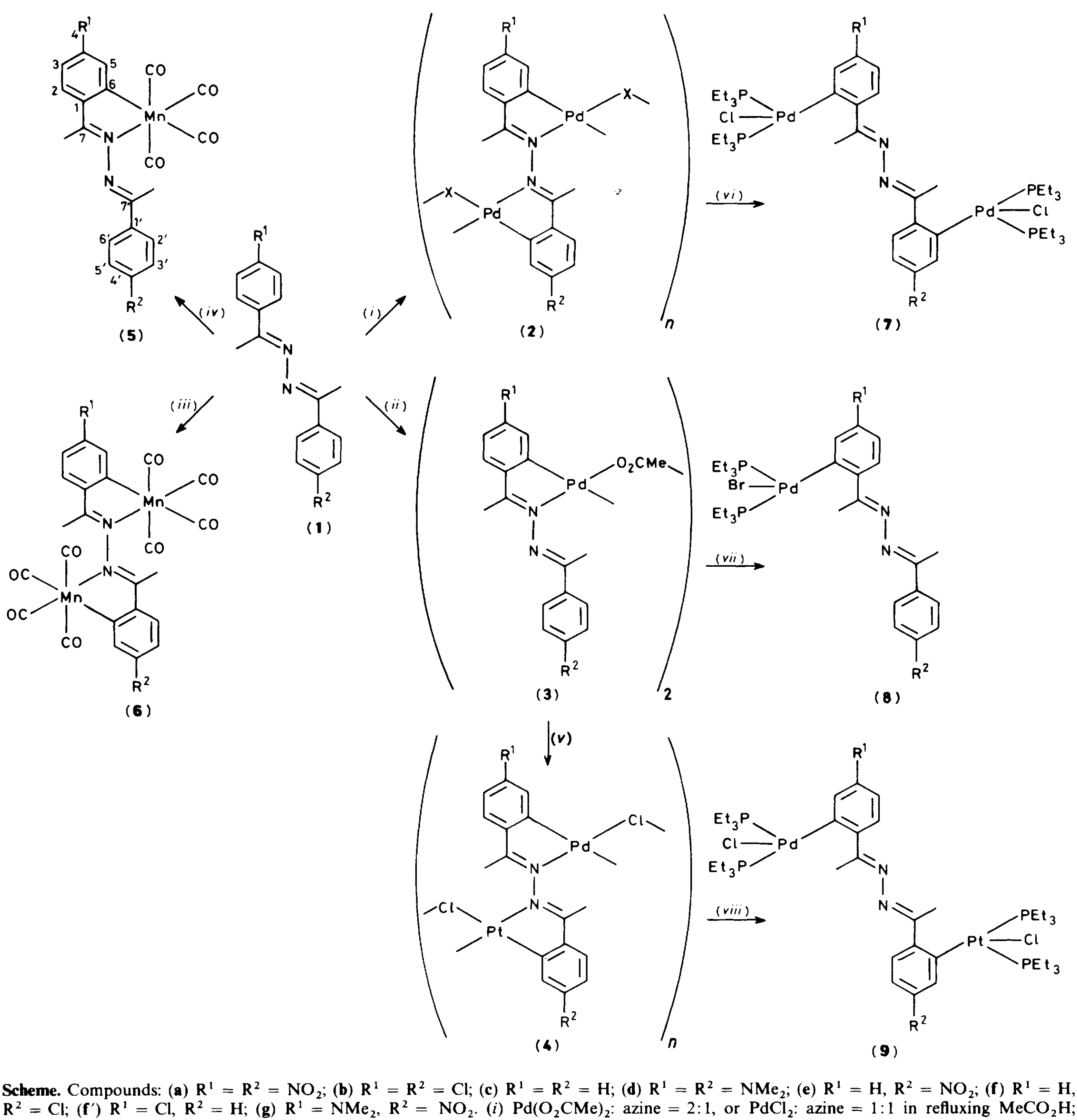
† (2-Benzylidenehydrazonomethylphenyl-C^1N)tetracarbonylmanganese(I).

Supplementary data available (No. SUP 56506, 5 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.



Scheme. Compounds: (**a**) $R^1 = R^2 = NO_2$; (**b**) $R^1 = R^2 = Cl$; (**c**) $R^1 = R^2 = H$; (**d**) $R^1 = R^2 = NMe_2$; (**e**) $R^1 = H$, $R^2 = NO_2$; (**f**) $R^1 = H$, $R^2 = Cl$; (**f′**) $R^1 = Cl$, $R^2 = H$; (**g**) $R^1 = NMe_2$, $R^2 = NO_2$. (*i*) $Pd(O_2CMe)_2$: azine = 2:1, or $PdCl_2$: azine = 1:1 in refluxing $MeCO_2H$; (*ii*) $Pd(O_2CMe)_2$: azine = 1:1, in refluxing $MeCO_2H$; (*iii*) $[MnMe(CO)_5]$: azine = 2:1, in refluxing octane; (*iv*) $[MnMe(CO)_5]$: azine = 1:1, in refluxing octane; (*v*) (**3b**) or (**3c**): $K_2[PtCl_4]$ = 1:1, in refluxing $MeCO_2H$; (*vi*) KCl and PEt_3 in acetone; (*vii*) LiBr and PEt_3 in acetone; (*viii*) PEt_3 or PPh_3 in chloroform

to $[\{Pd(p\text{-}RC_6H_3CH{=}N\text{-})(O_2CMe)\}_n]$ (**2a**)—(**2d**), dicyclometallated polymeric compounds. This is contrary to the results obtained with $PdCl_2$, where the azine (**1a**) gives a non-metallated compound and the azine (**1d**) is decomposed. If equimolar amounts (1:1) of $[Pd(O_2CMe)_2]$ and the azines (**1b**) or (**1c**) are used, the monocyclometallated compounds $[\{Pd(p\text{-}RC_6H_3CH{=}N\text{-}N{=}CHC_6H_4R\text{-}p)(O_2CMe)\}_2]$ [R = Cl (**3b**) or H (**3c**)] are obtained in each case as a mixture of *cis* and *trans* isomers.

By treatment of compounds (**3b**) and (**3c**) with $PtCl_4{}^{2-}$ the mixed-metal complexes $[\{ClPd(p\text{-}RC_6H_3CH{=}N\text{-}N{=}CHC_6H_3R\text{-}p)PtCl\}_n]$ [R = Cl (**4b**) or H (**4c**)] were obtained. The corresponding reactions with $[MnMe(CO)_5]$ in refluxing heptane for 24 h led only to decomposition of the organometallic compounds. Compounds (**4b**) and (**4c**) are the first binuclear cyclometallated compounds with two different metals.[15] It has been reported[5] that, when $[MnMe(CO)_5]$ is added to the monometallated compounds $[Pd(C_6H_4N{=}NPh)(C_5H_5)]$ or $[Rh(C_6H_4N{=}NPh)Cl]$, only ligand transfer takes place, giving $[Mn(C_6H_4N{=}NPh)(CO)_4]$ in good yields.

The behaviour shown by the benzalazines in the reaction with $Pd(O_2CMe)_2$ can be accounted for by the mechanism

Table 1. Analytical data, decomposition temperatures, i.r. and $^{31}P-\{^{1}H\}$ n.m.r. data

	Analysis (%)[a]				I.r. (cm^{-1})		
Compound	C	H	N	Decomp. temp. (°C)	ν_{asym}(C=N)	ν(CO)	δ(P)[b]/p.p.m.
(**3b**)	43.8 (43.5)	2.7 (2.7)	6.3 (6.3)		1 600 1 630	—	—
(**3c**)[c]	51.6 (51.6)	3.5 (3.8)	7.6 (7.5)		1 610 1 630	—	—
(**3e**)	46.0 (46.0)	3.1 (3.1)	10.0 (10.1)		—	—	—
(**3f**)	47.5 (47.2)	3.0 (3.2)	6.8 (6.8)		—	—	—
(**3g**)	48.0 (46.9)	4.0 (3.9)	12.6 (13.9)		—	—	—
(**5c**)[d]	57.3 (57.8)	3.1 (3.0)	7.4 (7.5)	102—104	1 590, 1 630	2 080m, 1 990—1 985s, 1 945m	—
(**5d**)	57.3 (57.4)	4.6 (4.6)	12.0 (12.2)	178—180	1 580, 1 610	2 080m, 1 990s, 1 980s, 1 940m	—
(**6c**)	49.7 (48.9)	1.8 (1.9)	5.2 (5.2)	124—126	1 590	2 080m, 2 000s, 1 960s, 1 945m	—
(**6d**)	50.1 (49.9)	3.2 (3.2)	8.9 (8.9)	190—191	1 580	2 060m, 1 980s, 1 950s, 1 910m	—
(**6c**)[e]	66.8 (66.7)	4.0 (4.0)	3.1 (2.8)	172—174	1 590	2 000s, 1 940s, 1 900s	—
(**7a**)	43.7 (43.4)	6.5 (6.5)	5.6 (5.3)	228—230	1 620	—	14.17
(**7d**)	48.7 (48.1)	7.7 (7.7)	5.7 (5.3)	240—242	1 610	—	12.32
(**7f**)	45.7 (45.8)	6.8 (7.0)	3.0 (2.8)	216—218		—	13.88[f] 13.60[g]
(**8b**)	44.6 (44.7)	5.7 (5.6)	3.6 (4.0)	151—152	1 615, 1 630	—	11.89
(**8c**)	49.5 (49.6)	6.7 (6.6)	4.3 (4.4)	174—175	1 610, 1 630	—	11.74
(**8e**)	46.3 (46.3)	5.9 (6.0)	6.0 (6.2)	132—135	—	—	11.69
(**8f**) + (**8f′**)	47.0 (47.0)	6.0 (6.1)	4.4 (4.2)	138—139	—	—	11.82, 11.65
(**8g**)	46.9 (46.8)	6.5 (6.3)	7.3 (7.8)	178—180	—	—	11.18
(**9c**)	44.0 (43.4)	6.8 (6.7)	2.6 (2.7)	158—160	1 610	—	13.77 (2 716),[h] 13.29
(**9c**)[i]	63.5 (63.5)	4.4 (4.3)	2.0 (1.7)	216—217	1 620	—	—
(**9b**)	40.4 (40.7)	6.0 (6.1)	2.5 (2.5)	218—220	1 610	—	13.58 (2 659),[h] 13.26
(**9b**)[i]	60.7 (60.9)	4.0 (4.0)	1.8 (1.6)	238—240	1 620	—	—

[a] Calculated values are given in parentheses. [b] Relative to H_3PO_4, in $CDCl_3$. [c] Previously reported, see ref. 11. [d] Previously reported, see ref. 10. [e] One CO replaced by PPh_3. [f] Assigned to P atoms of Cl-substituted ring. [g] Assigned to P atoms of unsubstituted ring. [h] J(P–Pt)/Hz in parentheses. [i] Analogous to compounds (**9c**) and (**9b**) but with PPh_3 instead of PEt_3.

proposed for the palladation of azobenzene,[16] *i.e.* co-ordination of the ligand to the metal followed by electrophilic attack of Pd^{II} on the aromatic ring. Thus, 24 h are necessary to obtain the dicyclometallated compound (**2a**), but (**2d**) is obtained in only 15 min, in agreement with the different activation to electrophilic attack produced by the substituents of the organic ligand.

We have also studied the action of $PdCl_2$ and $Pd(O_2CMe)_2$ on asymmetrically substituted benzalazines p-$R^1C_6H_4CH{=}N{-}N{=}CHC_6H_4R^2$-$p$ [R^1 = H, R^2 = NO_2 (**1e**); R^1 = H, R^2 = Cl (**1f**); R^1 = NMe_2, R^2 = NO_2 (**1g**)] in order to confirm the electrophilic character of the palladation of benzalazines, and to study the relative importance of the substituents in the reaction. We have used azines substituted in the *para* position, both to avoid the influence of steric effects on the reaction and because only compounds metallated at the C atom *meta* to the ring substituent can be formed. These asymmetric azines are less stable than the symmetric ones, and more easily undergo disproportionation and hydrolysis reactions, which explains why they sometimes decompose before metallation takes place.

The action of $Pd(O_2CMe)_2$ on the azines (**1e**) and (**1g**) in equimolar amounts, in anhydrous acetic acid under reflux, leads to the formation of the monometallated compounds $[\{Pd(C_6H_4CH{=}N{-}N{=}CHC_6H_4NO_2\text{-}p)(O_2CMe)\}_2]$ (**3e**) and $[\{Pd(p\text{-}Me_2NC_6H_3CH{=}N{-}N{=}CHC_6H_4NO_2\text{-}p)(O_2CMe)\}_2]$ (**3g**), in which the non-metallated ring contains the NO_2 substituent, in only 30 min. With an excess of $Pd(O_2CMe)_2$, decomposition of the asymmetric azines takes place before metallation of rings with NO_2 substituents is observed. Although p-nitrobenzalazine (**1a**) is metallated by $Pd(O_2CMe)_2$ the reaction takes 24 h; in such a long time, both the asymmetric azines (**1e**) and (**1g**) and the monometallated compounds (**3e**) and (**3g**) decompose. With $PdCl_2$ and azine (**1e**), a non-C-metallated compound is formed, and azine (**1g**)

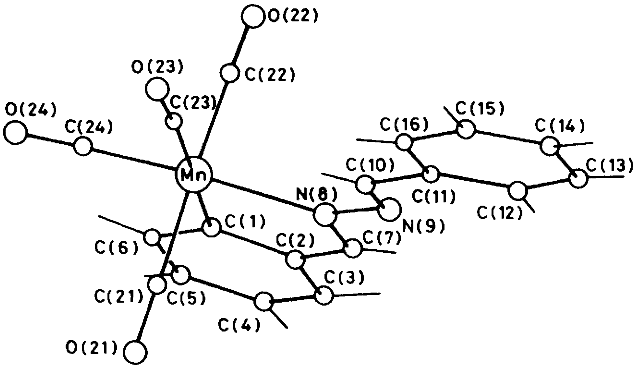


Figure. Molecular structure of $[\overline{\mathrm{Mn}(\mathrm{C_6H_4CH{=}N}}\mathrm{{-}N{=}CHPh)(CO)_4}]$ **(5c)**

decomposes under the same reaction conditions. In the case of azine **(1f)** in which the substituents have similar electronic properties, the action of $PdCl_2$ gives only the dicyclometallated polymer $[\{\mathrm{Cl}\overline{\mathrm{Pd}(p\text{-}\mathrm{ClC_6H_3CH{=}N}}\text{-}\overline{\mathrm{N{=}CHC_6H_4)Pd}}\mathrm{Cl}\}_n]$ **(2f)**, even with a deficiency of $PdCl_2$, similarly to the reactions with symmetric azines[12] and *N,N,N′,N′*-tetra-alkylxylenediamines,[7] which also give only the dicyclometallated compounds. $Pd(O_2CMe)_2$ leads to a mixture of $[\{\overline{\mathrm{Pd}(\mathrm{C_6H_4CH{=}N}}\mathrm{{-}N{=}CHC_6H_4Cl}\text{-}p)(\mathrm{O_2CMe})\}_2]$ **(3f)** and $[\{\overline{\mathrm{Pd}(p\text{-}\mathrm{ClC_6H_3CH{=}N}}\mathrm{{-}N{=}CHPh)(O_2CMe)}\}_2]$ **(3f′)**, the major component **(3f)** (60%) being that metallated in the more electron-rich ring.

Taking into account the effect of substituents, it can be stated that Pd^{II} acts as an electrophilic reagent towards the azine ligands.

Cyclometallation of N-donor ligands by manganese has been less studied than palladation reactions. A nucleophilic mechanism has been proposed for manganation of substituted azobenzenes,[8] but the preparation of cyclometallated complexes from $[MnMe(CO)_5]$ and azobenzenes activated with strong electron-donating groups NMe_2, EtO, and MeO, has also been reported.[10]

The action of $[MnMe(CO)_5]$ on the symmetric azines **(1a)**—**(1c)**, and **(1d)** in equimolar amounts, in refluxing octane for 6 h, has been studied. With **(1c)** and **(1d)** the monometallated compounds $[\overline{\mathrm{Mn}(p\text{-}\mathrm{RC_6H_3CH{=}N}}\mathrm{{-}N{=}CHC_6H_4R}\text{-}p)(\mathrm{CO})_4]$ [R = H **(5c)** or NMe_2 **(5d)**] were obtained. If an excess of $[MnMe(CO)_5]$ (1:3) is used the dimetallated complexes are obtained. No reaction was observed between $[MnMe(CO)_5]$ and *p*-nitrobenzalazine **(1a)**, the most activated azine towards nucleophilic reagents. In some cases, the metallation reactions afforded a mixture of the mono- and di-metallated compounds, which were readily separated by column chromatography over silica gel.

These results could be accounted for by an electrophilic mechanism; thus the azine with the electron-withdrawing substituent NO_2 is not metallated and that with the electron-donating substituent NMe_2 is metallated. However, the non-metallation of azine **(1a)** could also be attributed to its lower solubility in the solvent used, but the action of $[MnMe(CO)_5]$ on the asymmetric azine **(1e)** in octane, a solvent in which this azine is soluble, does not give metallation, neither in the NO_2-substituted ring nor in the unsubstituted. Thus, reactions of $[MnMe(CO)_5]$ with benzalazines do not seem to be nucleophilic, but it is not possible to propose an electrophilic mechanism, as clearly as with Pd^{II}.

Since the preparation of the first cyclometallated compound, obtained in 1963 by the action of $[Ni(\eta^5\text{-}C_5H_5)_2]$ on azobenzene,[3] only a few other nickel compounds of this class have been reported.[17] Bruce and co-workers,[18] studying cyclometallation reactions between benzylideneanilines and some metal complexes, did not observe any reaction between these ligands and nickelocene, although they are readily metallated by Pd^{II} and Mn^{I}. Attempts by us with benzalazines and several nickel compounds in a variety of solvents (benzene, acetic acid) were also unsuccessful.

From the results obtained on the metallation of benzalazines it can be suggested that the metallating capacity changes in the order $Pd(O_2CMe)_2 > PdCl_2 > PdCl_4^{2-} \gg NiX_2$ for metallic compounds of d^8 configuration. The higher ability of $Pd(O_2CMe)_2$ to cyclometallate azines is in accord with the fact that less strenuous conditions are needed, and so it is possible to metallate azines of low stability such as **(1d)**, which decompose in the reaction with $PdCl_2$. With $Pd(O_2CMe)_2$, metallation of azine **(1a)** is accomplished, but with $PdCl_2$ only a non-C-metallated compound is obtained. With $PtCl_4^{2-}$, only azine **(1b)** is metallated since longer reaction times are needed and azines **(1c)**, **(1d)**, and **(1f)** decompose.[14]

Although metallation by Mn^{I} takes place under conditions different from those used for palladation and platination, $[MnMe(CO)_5]$ can be considered a good metallating agent. Another factor to take into account is the stability of the ligands under the reaction conditions. Thus, if electron-donating substituents such as NMe_2, and even H, favour the electrophilic attack, they also favour the decomposition processes, and when the metallic salt does not possess a good metallating capacity, decomposition of the ligands takes place before metallation (see the results with $PdCl_2$ [12] and $PtCl_4^{2-}$ [14]). However, if the azine is stabilized by formation of the monometallated compound, *i.e.* $[\{\overline{\mathrm{Pd}(\mathrm{C_6H_4CH{=}N}}\mathrm{{-}N{=}CHPh)(O_2CMe)}\}_2]$, metallation of the unsubstituted ring by $PtCl_4^{2-}$ takes place giving $[\{\mathrm{Cl}\overline{\mathrm{Pd}(\mathrm{C_6H_4CH{=}N}}\text{-}\overline{\mathrm{N{=}CHC_6H_4)Pt}}\mathrm{Cl}\}_n]$.

In conclusion, the results obtained with benzalazines show that the mechanisms proposed for the metallation of azobenzenes,[8] in which Pd^{II} acts as an electrophilic reagent and Mn^{I} as a nucleophilic one, cannot be wholly extended to the metallation of all N-donor ligands.

Characterization of Compounds.—The monomeric cyclomanganated compounds are sufficiently soluble to be characterized, but the polymeric and dimeric cyclopalladated compounds are insoluble and must be treated with phosphines to obtain soluble compounds, which can be more easily characterized by n.m.r. spectroscopy.

The action of an excess of PEt_3 on acetone solutions of the cyclometallated complexes gives compounds of general formulae $[Pd(p\text{-}R^1C_6H_3CH{=}N\text{-}N{=}CHC_6H_4R^2\text{-}p)Br(PEt_3)_2]$ **(8)** and $[(Et_3P)_2ClM^1(p\text{-}R^1C_6H_3CH{=}N\text{-}N{=}CHC_6H_3R^2\text{-}p)\text{-}M^2Cl(PEt_3)_2]$ **(7)** and **(9)** (see Scheme). An excess of PPh_3 with $[\{\overline{\mathrm{Mn}(\mathrm{C_6H_4CH{=}N}}\text{-})(\mathrm{CO})_4\}_2]$ gives the mono(triphenylphosphine) derivative $[\{\overline{\mathrm{Mn}(\mathrm{C_6H_4CH{=}N}}\text{-})\}_2(\mathrm{CO})_3(\mathrm{PPh_3})]$.

Analytical data and decomposition temperatures are given in Table 1. The compounds are air-stable solids, but they decompose slowly in chloroform, especially those of manganese. The low values of the molar conductivity in anhydrous acetone (10^{-4} mol dm^{-3}) at 20 °C (1—4 Ω^{-1} cm^2 mol^{-1}) indicate their non-electrolytic character. The magnetic measurements at room temperature indicate a diamagnetic behaviour as expected for a d^8 configuration, Pd^{II}, in a square-planar arrangement, and for a low-spin d^6 configuration, Mn^{I}, in an octahedral arrangement.

The position of $\nu_{asym}(C{=}N)$ for metallated compounds of the symmetric azines is given in Table 1. Mono- or dimetallation is clearly revealed in the $\nu_{asym}(C{=}N)$ region. For dimetallated compounds only one band is observed, but for the monometallated compounds two bands are observed. It should

Table 2. Proton n.m.r. data[a]

Compound	Azomethine protons[b]	Aromatic protons[b,c]
(3b)[d]	*cis* 8.07 (s, H^{7}), 8.67 (s, H$^{7'}$) *trans* 7.74 (s, H^{7}), 8.61 (s, H$^{7'}$)	6.71—7.64 (m, 14 H)
(3c)[d]	*cis* 8.09 (s, H^{7}), 8.78 (s, H$^{7'}$) *trans* 7.80 (s, H^{7}), 8.68 (s, H$^{7'}$)	6.64—7.63 (m, 18 H)
(5c)	8.55 (s, H^{7}), 8.66 (s, H$^{7'}$)	7.19 (m), 7.34 (m), 7.52 (m), 7.86 (br s, H^{2}), 8.03 (d, 7.0, H^{5})
(5d)	8.41 (s, H^{7}), 8.53 (s, H$^{7'}$)	6.46 (d, 8.6, H^{3}), 6.72 (d, 8.3, H$^{3'}$, H$^{5'}$), 7.31 (s, H^{5}), 7.43 (d, 8.6, H^{2}), 7.69 (d, 8.3, H$^{2'}$, H$^{6'}$)
(6c)	8.46 (s, H^{7})	7.24 (t, 7.3, H^{3}), 7.40 (t, 7.3, H^{4}), 7.72 (d, 7.6, H^{2}), 8.01 (d, 7.6, H^{5})
(6d)	8.20 (s, H^{7})	6.47 (dd, 8.6, 2.5,[e] H^{3}), 7.22 (d, 2.5,[e] H^{5}), 7.49 (d, 8.6, H^{2})
(7a)	9.48 (s, H^{7})	7.86 (d, 7.2, H^{3}), 8.03 (7.2, H^{2}), 8.30 (s, H^{5})
(7d)	9.16 (s, H^{7})	6.45 (d, 8.3, H^{3}), 6.80 (s, H^{5}), 7.72 (d, 8.3, H^{2})
(7f)	9.30 (s, H^{7}), 9.34 (s, H$^{7'}$)	7.00 (m), 7.40 (s), 7.48 (m)
(8b)	9.24 (s, H^{7}), 8.71 (s, H$^{7'}$)	7.00 (d), 7.42 (d), 7.47 (m), 7.77 (d)
(8c)	9.30 (s, H^{7}), 8.76 (s, H$^{7'}$)	7.05 (m), 7.45 (m), 7.84 (m)
(8e)	9.35 (s, H^{7}), 8.82 (s, H$^{7'}$)	7.08 (m, H^{4}, H^{5}), 7.51 (d, 7.6, H^{3}), 7.76 (d, 7.6, H^{6}), 8.00 (d, 9.0, H$^{2'}$, H$^{6'}$), 8.30 (d, 8.9, H$^{3'}$, H$^{5'}$)
(8f) + **(8f′)**[f]	**(8f)** 9.24 (s, H^{7}), 8.76 (s, H$^{7'}$) **(8f′)** 9.29 (s, H^{7}), 8.71 (s, H$^{7'}$)	7.05 (m), 7.40 (m), 7.80 (m)
(8g)	9.25 (s, H^{7}), 8.76 (s, H$^{7'}$)	6.43 (dd, 7.8, H^{3}), 6.83 (s, H^{5}), 7.75 (d, 7.8, H^{2}), 7.96 (d, 8.9, H$^{2'}$, H$^{6'}$), 8.72 (d, 8.9, H$^{3'}$, H$^{5'}$)
(9b)	9.31 (s, H^{7}), 9.48 (t, H$^{7'}$)[g]	6.96 (m), 7.42 (s), 7.54 (s), 7.81 (m)
(9c)	9.35 (s, H^{7}), 9.53 (t, H$^{7'}$)[g]	6.98 (m), 7.45 (m), 7.52 (m), 7.86 (m)

[a] In $CDCl_3$, chemical shifts in p.p.m. (δ) with respect to internal $SiMe_4$. [b] Assignments are given in parentheses. See Scheme for numbering sequence. [c] ^{3}J(HH) are given in parentheses. [d] δ(CH_3COO): *cis* 1.85 (s), 2.36 (s); *trans* 2.05 (s). [e] ^{4}J(HH). [f] See text. [g] J(Pt–H) = 11 Hz.

Table 3. ^{13}C-{^{1}H} n.m.r. data[a]

Compound	Azomethine carbons[b]		Aromatic carbons[b]					
(5c)	172.5 (C^{7})	160.4 (C$^{7'}$)	[145.7	131.4	124.3	130.2	141.8][c]	179.5 (C^{6})
			133.1 (C$^{1'}$)	129.1 (C$^{2'}$)	129.0 (C$^{3'}$)	132.8 (C$^{4'}$)	129.0 (C$^{5'}$)	129.1 (C$^{6'}$)
(6c)	172.7 (C^{7})	—	[—	132.5	124.6	131.6	141.5][c]	
			—	—	—	—	—	
(5d)	169.7 (C^{7})	160.4 (C$^{7'}$)	[—		144.5	149.8	156.0][c]	—
			122.4 (C$^{1'}$)	129.6 (C$^{2'}$)	111.6 (C$^{3'}$)	130.7 (C$^{4'}$)	111.6 (C$^{5'}$)	129.6 (C$^{6'}$)
(6d)	169.5 (C^{7})	—	[—	122.4	131.4	132.7	151.8][c]	185.0 (C^{6})
			—	—	—	—	—	—
(7a)	164.2 (C^{7})	—	127.8 (C^{1})	128.4 (C^{2})	108.1 (C^{3})	150.1 (C^{4})	118.8 (C^{5})	160.0 (C^{6})
			—	—	—	—	—	—
(7d)	166.1 (C^{7})	—	144.0 (C^{1})	127.0 (C^{2})	118.1 (C^{3})	147.0 (C^{4})	130.6 (C^{5})	163.5 (C^{6})
			—	—	—	—	—	—
(8b)	166.7 (C^{7})	160.3 (C$^{7'}$)	136.9 (C^{1})	128.6 (C^{2})	123.5 (C^{3})	135.4 (C^{4})	136.1 (C^{5})	164.4 (C^{6})
			132.8 (C$^{1'}$)	129.5 (C$^{2'}$)	129.0 (C$^{3'}$)	136.6 (C$^{4'}$)	129.0 (C$^{5'}$)	129.5 (C$^{6'}$)
(8e)	169.4 (C^{7})	158.7 (C$^{7'}$)	137.8 (C^{1})	128.3 (C^{2})	123.3 (C^{3})	130.0 (C^{4})	137.2 (C^{5})	163.4 (C^{6})
			140.4 (C$^{1'}$)	128.9 (C$^{2'}$)	123.9 (C$^{3'}$)	148.9 (C$^{4'}$)	123.9 (C$^{5'}$)	128.9 (C$^{6'}$)
(8g)	169.7 (C^{7})	156.2 (C$^{7'}$)	126.4 (C^{1})	129.5 (C^{2})	108.0 (C^{3})	150.7 (C^{4})	118.8 (C^{5})	165.3 (C^{6})
			141.2 (C$^{1'}$)	128.3 (C$^{2'}$)	123.7 (C$^{3'}$)	148.9 (C$^{4'}$)	123.7 (C$^{5'}$)	128.3 (C$^{6'}$)

[a] In $CDCl_3$; chemical shifts in p.p.m. (δ) with respect to internal $SiMe_4$. [b] See Scheme for numbering sequence. [c] Not unambiguously assigned.

be noted that the frequency of these bands for the metallated compounds is smaller than those for free azines, even with compounds (**7**)—(**9**) in which there are apparently no Pd–N bonds, suggesting that there is some degree of interaction between these atoms, a fact which has been confirmed by an *X*-ray analysis of $[\{(Et_3P)_2ClPd(p\text{-}ClC_6H_3CH{=}N\text{-})\}_2]$.[12] For metallated compounds of asymmetric azines this region (1 580—1 630 cm^{-1}) is too complex and ν(C=N) cannot be assigned. The i.r. spectra of compounds (**2**) and (**3**) show two bands at 1 580 and 1 420 cm^{-1} which are typical of bridging acetate. Compounds (**7**)—(**9**) show bands typical of coordinated triethylphosphine.[19] The i.r. spectra of (**5**) and (**6**) in the ν(CO) region are typical of a *cis*-$M(CO)_4LL'$ derivative.

The proton n.m.r. data for the metallated compounds are in Table 2. It is to be noted that in compounds of symmetric azines the appearance of two or one azomethine signals for each compound supports a mono- or di-palladated structure. The chemical shifts of the azomethine protons near the metallated ring, in the triethylphosphine-containing compounds, appear at lower field than those of the free azines, in agreement with the close vicinity of the hydrogen and metal atoms which gives rise to a large paramagnetic shift of such protons. The spectra of the mixed-metal compounds (**9b**) and (**9c**) show two azomethine signals for each compound.[15] The protons near the platinum appear as a pseudo-triplet due to coupling with ^{195}Pt [J(PtH) = 11 Hz]. For asymmetric azines, two signals due to the non-equivalent azomethine protons are observed, *e.g.* at 8.55 and 8.60 p.p.m. for $p\text{-}ClC_6H_4CH{=}N\text{-}N{=}CHPh$. These signals appear at lower field for compound (**7f**), showing clearly that metallation in both rings has taken place. The spectrum of the mixture of (**8f**) and (**8f′**) shows four signals in the azomethine region; 60% metallation at the unsubstituted ring and 40% at the chloro-substituted ring occurs. The spectra of monomeric compounds of the other asymmetric azines, *i.e.* (**8e**) and (**8g**), show that in both cases palladation takes place only in the more electron-rich aromatic ring.

For the cyclometallated compounds (**5**) and (**6**) the azomethine protons near the metallated ring appear at higher field than those in the free azines.[20] Four signals appear for compounds (**3**), two of them corresponding to the *cis* isomer and two to the *trans* isomer, as pointed out by Thomson and Heck.[11] From the relative intensities the solution was calculated to contain 70% of the *trans* isomer in each case.

As far as the $MCl(PEt_3)_2$ group itself is concerned, the methyl signals appear as quintuplets, which is typical of a *trans* arrangement of the two phosphines due to the so-called 'virtual coupling' [δ(P–CH_3) 1.04]. The signals due to the aromatic protons are also reported in Table 2. In most cases their unequivocal assignment is possible, based on the observed coupling constants and on the influence of the different substituents in the aromatic ring.

Table 4. Principal bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for complex (**5c**)

C(1)–Mn	2.068(5)	N(9)–N(8)	1.393(6)
N(8)–Mn	2.120(5)	C(10)–N(9)	1.268(9)
C(21)–Mn	1.857(7)	C(11)–C(10)	1.471(9)
C(22)–Mn	1.879(7)	C(12)–C(11)	1.359(10)
C(23)–Mn	1.853(7)	C(16)–C(11)	1.384(9)
C(24)–Mn	1.789(8)	C(13)–C(12)	1.403(9)
C(2)–C(1)	1.389(9)	C(14)–C(13)	1.374(11)
C(6)–C(1)	1.379(9)	C(15)–C(14)	1.342(12)
C(3)–C(2)	1.405(8)	C(16)–C(15)	1.393(11)
C(7)–C(2)	1.446(9)	O(21)–C(21)	1.127(7)
C(4)–C(3)	1.397(9)	O(22)–C(22)	1.140(8)
C(5)–C(4)	1.363(11)	O(23)–C(23)	1.124(8)
C(6)–C(5)	1.399(10)	O(24)–C(24)	1.124(8)
N(8)–C(7)	1.295(8)		

N(8)–Mn–C(1)	79.3(2)	C(5)–C(4)–C(3)	119.6(6)
C(21)–Mn–C(1)	83.3(2)	C(6)–C(5)–C(4)	123.2(6)
C(21)–Mn–N(8)	89.1(2)	C(5)–C(6)–C(1)	118.6(7)
C(22)–Mn–C(1)	84.7(2)	N(8)–C(7)–C(2)	117.7(6)
C(22)–Mn–N(8)	89.7(2)	C(7)–N(8)–Mn	113.8(4)
C(22)–Mn–C(21)	167.9(2)	N(9)–N(8)–Mn	135.5(4)
C(23)–Mn–C(1)	177.6(3)	N(9)–N(8)–C(7)	110.6(5)
C(23)–Mn–N(8)	102.4(3)	C(10)–N(9)–N(8)	117.4(5)
C(23)–Mn–C(21)	94.9(3)	C(11)–C(10)–N(9)	120.0(6)
C(23)–Mn–C(22)	97.1(3)	C(12)–C(11)–C(10)	123.3(6)
C(24)–Mn–C(1)	90.2(2)	C(16)–C(11)–C(10)	117.5(6)
C(24)–Mn–N(8)	169.5(2)	C(16)–C(11)–C(12)	119.1(6)
C(24)–Mn–C(21)	88.9(3)	C(13)–C(12)–C(11)	121.7(7)
C(24)–Mn–C(22)	90.1(3)	C(14)–C(13)–C(12)	117.7(7)
C(24)–Mn–C(23)	88.1(3)	C(15)–C(14)–C(13)	121.3(7)
C(2)–C(1)–Mn	112.5(4)	C(16)–C(15)–C(14)	120.8(7)
C(6)–C(1)–Mn	129.2(5)	C(15)–C(16)–C(11)	119.3(8)
C(6)–C(1)–C(2)	118.2(5)	O(21)–C(21)–Mn	175.7(5)
C(3)–C(2)–C(1)	123.6(6)	O(22)–C(22)–Mn	175.4(5)
C(7)–C(2)–C(1)	116.6(5)	O(23)–C(23)–Mn	173.7(7)
C(7)–C(2)–C(3)	119.8(6)	O(24)–C(24)–Mn	177.6(7)
C(4)–C(3)–C(2)	116.8(6)		

The $^{31}P-\{^1H\}$ n.m.r. spectra of PEt_3-containing compounds confirm the *trans* arrangement of the phosphine ligands. The chemical shifts and the coupling constants are reported in Table 1.

The $^{13}C-\{^1H\}$ n.m.r. spectra and the proposed assignments are summarized in Table 3. For the palladium compounds, all the signals of the aromatic, methine, and triethylphosphine carbons are clearly seen. The metallated carbon atom is shifted downfield by 30—35 p.p.m. in relation to its position in the free azine and it appears as a triplet due to coupling with the two equivalent phosphorus atoms in a *trans* arrangement [^2J(PC) = 6 Hz]. The high-field resonances were assigned to the ethyl groups of PEt_3. The methylene carbons appear as a triplet at 15.00 p.p.m., as a result of the 'virtual coupling' with the phosphorus atoms; the methyl carbons appear as a singlet at 8.00 p.p.m., confirming the *trans* arrangement of these ligands. Careful measurement of the ^{13}C n.m.r. spectra of the complexes (**5**) and (**6**) did not resolve all the expected lines. The metallated carbon atoms seem to be resolved only in complexes (**6d**) and (**5c**) and show large downfield shifts, *ca.* 50 p.p.m. The carbonyls occur as broad, low-intensity peaks, at *ca.* 220.0 and 213.0 p.p.m.

The crystal structure of $[\overline{Mn(C_6H_4CH=N}-N=CHPh)(CO)_4]$ (**5c**) is composed of discrete molecules separated by van der Waals distances (Figure). Selected bond lengths and angles are listed in Table 4.

The manganese atom is co-ordinated in a distorted octahedral configuration with the chelate ligand and two carbonyl ligands in the equatorial plane, while the apical positions are occupied by the other two carbonyl ligands. The ligand is attached *via* a metal–nitrogen bond and a metal–carbon σ bond to the *ortho* position of one benzalazine ring.

On the whole, the conformation of the co-ordinated ligand closely resembles that of the free benzalazine.[21] The five-membered ring Mn–N(8)–C(7)–C(2)–C(1) is planar, owing to the restricted rotation about the C(1)–C(2) and C(7)=N(8) bonds as in $[\overline{Mn(C_6H_4CH=N}Ph)(CO)_4]$;[22] N(9),C(10), and the C(11) phenyl moiety are contained in the same plane. The torsion angle C(7)–N(8)–N(9)–C(10) is −172.4(5)°. The C(7)=N(8) bond is slightly lengthened due to co-ordination, 1.295(8) Å, compared with the non-co-ordinated C(10)=N(9), 1.268(9) Å, and in the free ligand, 1.270 Å. The Mn–N(8) bond produces a decrease in the angle C(1)–C(2)–C(7), 116.6(5)°, which is less than C(10)–C(11)–C(12), 123.3(6)°.

The Mn–C(1) bond distance [2.068(5) Å] is identical within experimental error to the Mn–C distance [2.060(8) Å] found in $[\overline{Mn(C_6H_4CH=N}Ph)(CO)_4]$, and slightly shorter than the

Table 5. Positional parameters (× 10^4) for non-hydrogen atoms with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Mn	12 571(6)	20 695(4)	16 851(11)	C(13)	1 050(6)	4 265(4)	−3 145(9)
C(1)	1 275(4)	1 095(2)	1 288(7)	C(14)	1 120(6)	4 871(3)	−2 593(10)
C(2)	1 268(5)	1 002(3)	175(7)	C(15)	1 304(6)	4 941(4)	−1 304(10)
C(3)	1 251(5)	385(3)	−336(9)	C(16)	1 385(6)	4 399(3)	−533(10)
C(4)	1 262(6)	−156(3)	360(9)	C(21)	−157(5)	1 958(3)	−175(8)
C(5)	1 302(5)	−65(3)	1 493(9)	O(21)	−1 005(4)	1 850(3)	−1 284(7)
C(6)	1 311(5)	552(3)	1 985(9)	C(22)	2 695(5)	1 992(2)	3 522(8)
C(7)	1 262(5)	1 583(3)	−489(8)	O(22)	3 559(4)	1 902(3)	4 641(7)
N(8)	1 272(4)	2 141(2)	8(6)	C(23)	1 198(6)	2 936(3)	2 027(9)
N(9)	1 244(4)	2 649(3)	−770(6)	O(23)	1 167(5)	3 441(2)	2 334(8)
C(10)	1 369(5)	3 223(4)	−257(9)	C(24)	1 229(5)	1 852(3)	3 039(8)
C(11)	1 307(4)	3 782(3)	−1 072(7)	O(24)	1 247(5)	1 709(3)	3 932(7)
C(12)	1 120(5)	3 720(3)	−2 380(8)				

value predicted[23] for a single Mn–C(sp^2) bond. The Mn–N(8) bond distance [2.120(5) Å] is longer than in $[Mn(C_6H_4CH=NPh)(CO)_4]$, 2.070(7) Å, and longer than that estimated[22] for a Mn–N(sp^2) single bond. The Mn–CO bond distances, average 1.84(3) Å, are similar to those found in analogous compounds;[22] Mn–C(24), is the shortest, consistent with a smaller *trans* influence of the nitrogen atom.

The co-ordination about the manganese atom is distorted octahedral, the major distortions being related to the angle C(1)–Mn–N(8) 79.3(2)° and C(23)–Mn–N(8) 102.4(3)°. The decrease in C(1)–Mn–N(8) is produced by co-ordination of the chelate ligand to the metal; the lengthening of C(23)–Mn–N(8) is produced by steric effects between the C(23) carbonyl ligand and the non-metallated part of the azine.

Experimental

N.m.r. spectra were obtained on a Varian XL (^1H, 200 MHz; ^{13}C, 50.3 MHz; ^{31}P, 80.98 MHz) spectrometer, i.r. spectra on a Beckman IR-20A spectrophotometer for KBr discs or heptane solutions (2 100—1 900 cm^{-1}). Microanalyses were performed by the Institut de Química Bio-Orgànica de Barcelona (C.S.I.C.).

Crystallography.—*Crystal data.* $C_{18}H_{11}MnN_2O_4$, M = 374.24, monoclinic, a = 20.591(3), b = 20.517(3), c = 12.466(2) Å, β = 140.78(2)°, U = 3 330(1) Å^3, space group $C2/c$, Z = 8, D_c = 1.492 g cm^{-3}, $F(000)$ = 1 520, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 8.59 cm^{-1}, room temperature.

Data collection. A yellow prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a Philips PW-1100 four-circle diffractometer. The unit-cell parameters were determined from 25 reflections ($4 \leqslant \theta \leqslant 9°$) and refined by least squares. Intensities were measured with graphite-monochromated Mo-K_α radiation, using the ω-scan technique with scan width 1° and scan speed 0.03° s^{-1}. Three reflections were measured every 2 h as orientation and intensity control, but significant variations were not observed. 1 940 Reflections were measured in the range $2 \leqslant \theta \leqslant 29.5°$, 1 896 of which were assumed as observed [$I \geqslant 2.5\sigma(I)$]. Lorentz-polarization, but not absorption corrections were made.

Structure solution and refinement. The structure was solved by direct methods, using the MULTAN system of computer programs[24] and refined isotropically and anisotropically by full-matrix least squares using the SHELX 76 computer program.[25] The function minimized was $w||F_o| - |F_c||^2$, where $w = [\sigma^2(F_o) + 0.072|F_o|^2]^{-1}$; f, f', and f'' were taken from ref. 26. All hydrogen atoms were located from a difference synthesis and refined with an overall isotropic thermal parameter, and the remaining atoms anisotropically. The final R was 0.059 (R' = 0.069).

Materials.—Solvents were dried and distilled before use. Symmetric azines were prepared according to published methods.[27] Asymmetric azines, p-$O_2NC_6H_4CH=N-N=CHPh$ and p-$O_2NC_6H_4CH=N-N=CHC_6H_4NMe_2$-$p$, were obtained by shaking a solution of p-nitrobenzaldehyde hydrazone and benzaldehyde or p-dimethylaminobenzaldehyde. p-Nitrobenzaldehyde hydrazone was prepared by the reaction of p-nitrobenzaldehyde with a 10—20 fold molar excess of 85% hydrazine hydrate in ethanol.[28] The azine p-$ClC_6H_4CH=N-N=CHPh$ was obtained from p-chlorobenzaldehyde hydrazone and benzaldehyde in ethanol. Due to the ease of formation of the corresponding symmetric azine from hydrazones and the tendency of these azines to undergo disproportionation reactions, (p-$ClC_6H_4CH=N-)_2$ and $(PhCH=N-)_2$ were formed during the synthesis and were separated by taking advantage of their different solubilities in chloroform. The purity of the ligand was checked by gas chromatography.

Synthesis of Cyclometallated Dimeric Compounds, $[\{Pd(p\text{-}R^1C_6H_3CH=N-N=CHC_6H_4R^2\text{-}p)(O_2CMe)\}_2]$ **(3b)**, **(3c)**, **(3e)**—**(3g)**.—A stirred suspension of $Pd(O_2CMe)_2$ (3.0 mmol, 0.67 g) in anhydrous acetic acid (15 cm^3) was treated with the appropriate azine **(1)** (3.2 mmol), under reflux for 15—45 min. The suspension was cooled, and the precipitate filtered off and recrystallized from toluene. Reaction times (min) and yields (%) obtained are: **(3b)**, 45, 80; **(3c)**, 30, 70; **(3e)**, 30, 70; **(3f)** + **(3f′)**, 30, 60; and **(3g)**, 15, 75.

Synthesis of Cyclometallated Polymeric Compounds, $[\{Pd(p\text{-}RC_6H_3CH=N-)(O_2CMe)\}_n]$ **(2a)**—**(2d)**.—A stirred suspension of $Pd(O_2CMe)_2$ (2.0 mmol, 0.45 g) in anhydrous acetic acid (20 cm^3) was treated with 1 mmol of the appropriate azine **(1)** and refluxed for 24 h; only 15 min are required with azine **(1d)**. The solids obtained were used in the following reactions without further purification.

$[\{ClPd(p\text{-}ClC_6H_3CH=N-N=CHC_6H_4)PdCl\}_n]$ **(2f)**. A mixture of $PdCl_2$ (2.0 mmol, 0.35 g) and the azine **(1f)** (3.0 mmol, 0.72 g) was stirred in anhydrous acetic acid (25 cm^3) under reflux for 24 h. After cooling, the yellow-green residue was filtered off and washed with chloroform and toluene. The solid obtained (0.4 g) was used in the following reactions without further purification.

$[\{ClPd(p\text{-}RC_6H_3CH=N-N=CHC_6H_3R\text{-}p)PtCl\}_n]$ **(4b)** *and* **(4c)**. A mixture of compound **(3b)** or **(3c)** (0.5 mmol) and $K_2[PtCl_4]$ (1.2 mmol, 0.49 g) in anhydrous acetic acid (20 cm^3) was refluxed for 24 h. The brown precipitate was filtered off and used in the following reactions without further purification.

Synthesis of Cyclometallated Monomeric Compounds, $[Mn(p\text{-}RC_6H_3CH=N-N=CHC_6H_4R\text{-}p)(CO)_4]$ **(5c)** *and* **(5d)**.—A solution of $[MnMe(CO)_5]$ (1.5 mmol, 0.31 g) and the benzalazine **(1c)** or **(1d)** (1.5 mmol) in octane (35 cm^3) was refluxed under nitrogen for 6 h. Recrystallization and separation by chromatography over silica gel, with $CHCl_3$ as the eluant, gave the yellow products (yield 50%).

$[\{Mn(p\text{-}RC_6H_3CH=N-)(CO)_4\}_2]$ **(6c)** *and* **(6d)**. A mixture of $[MnMe(CO)_5]$ (1.5 mmol, 0.31 g) and benzalazine **(1c)** or **(1d)** (0.5 mmol) was refluxed in octane (40 cm^3) under nitrogen for 9 h and then filtered. In the case of azine **(1c)**, chromatography of the concentrated solution with chloroform afforded the complex **(6c)**, 45% yield. With azine **(1d)**, the filtered solution was concentrated *in vacuo*, and the yellow-orange product was recrystallized from toluene–heptane giving **(6d)** in 60% yield.

Reactions with Phosphines.—*Preparation of* $[Pd(p\text{-}R^1C_6H_3CH=N-N=CHC_6H_4R^2\text{-}p)Br(PEt_3)_2]$ **(8b)**, **(8c)**, **(8e)**—**(8g)**. A mixture of the appropriate compound **(3)** (0.5 mmol), PEt_3 (3 mmol), and LiBr (0.12 g, 1.5 mmol) in acetone (40 cm^3) was shaken under nitrogen for 2 h and then filtered. The filtrate was concentrated *in vacuo* and ethanol was added. Recrystallization from chloroform–ethanol gave the product in *ca.* 70% yield.

$[\{(Et_3P)_2ClPd(p\text{-}RC_6H_3CH=N-)\}_2]$ **(7a)**—**(7d)**. A suspension of the appropriate compound **(2)** (*ca.* 0.5 mmol) in chloroform (20 cm^3) was treated with KCl (0.11 g, 1.5 mmol), and PEt_3 (3 mmol), and the mixture was shaken for 3 h. The solution was concentrated *in vacuo* and ethanol was added. The precipitate was collected and recrystallized from $CHCl_3$–EtOH to afford *ca.* 0.30 g of product.

$[(Et_3P)_2ClPd(p\text{-}ClC_6H_3CH=N-N=CHC_6H_4)PdCl(PEt_3)_2]$ **(7f)**. A stirred suspension of compound **(2f)** (0.52 g) in chloroform (20 cm^3) was treated with PEt_3 (5 mmol); the mixture was stirred for 2 h under nitrogen. After filtering off the solid, the filtrate was concentrated *in vacuo* and ethanol was added.

The orange solid residue was recrystallized from chloroform affording *ca.* 0.30 g of product.

$[(Et_3P)_2ClPd(p\text{-}RC_6H_3CH{=}N{-}N{=}CHC_6H_3R\text{-}p)PtCl(PEt_3)_2]$ (**9b**) and (**9c**). A suspension of compound (**4b**) or (**4c**) (0.64 g, 0.57 g) in chloroform (20 cm^3) was treated with PEt_3 (4 mmol) under N_2 and the mixture stirred at room temperature for 2 h. The solution was concentrated *in vacuo* and methanol was added. The residue was recrystallized and purified by column chromatography over silica gel, with $CHCl_3$ as the eluant, to give *ca.* 0.20 g of product.

$[(Ph_3P)_2ClPd(p\text{-}RC_6H_3CH{=}N{-}N{=}CHC_6H_3R\text{-}p)PtCl(PPh_3)_2]$. To a suspension of compound (**4b**) or (**4c**) (0.64 g, 0.57 g) in chloroform (30 cm^3) was added PPh_3 (1.05 g, 4 mmol) and the mixture refluxed for 1 h. The precipitate was filtered off and recrystallized from CH_2Cl_2–EtOH to give *ca.* 0.30 g of product.

$[\{\overline{Mn(C_6H_4CH{=}N}{-})(CO)_3(PPh_3)\}_2]$. Compound (**6c**) (0.27 g, 0.5 mmol) and PPh_3 (0.26 g, 1 mmol) in heptane (25 cm^3) were refluxed for 1 h. The solution was concentrated *in vacuo* and the residue recrystallized from chloroform, to give the product in 80% yield.

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