Precious metal polymers: platinum or gold atoms in the backbone

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The synthesis and characterisation of oligomers and polymers containing gold or platinum atoms in the backbone are reported. The polymers range in structure from the conjugated, rigid-rod type containing linear gold(1) centres to hyperbranched or dendrimeric materials containing octahedral platinum(1v) centres.

Introduction

This article gives a personal account of the synthesis and characterization of some new types of oligomers and polymers with either platinum or gold atoms in the chain backbone. These form a small part of the more general field of metal-containing polymers, which are of interest since they might have unusual optical or electrical properties or they might be useful as precursors to other materials or as catalyst precursors. There are several known types of linear-chain polynuclear coordination complexes containing platinum or gold, including the stacked, dimensional conductors semiconductors one or $K_2Pt(CN)_4Br_{0.30}\cdot 3H_2O,^1$ [Pt(NH₂Et)₄][PtCl₂(NH₂Et)₄]Cl₄· $4H_2O$ and $K_4[Pt_2(P_2O_5H_2)_4X] \cdot nH_2O$ (X = Cl, Br, I),² and the simple halogen-bridged gold(I) halides.³ More recently, rigid rod polymers such as $[Pt(PBu_3)_2(\mu-C\equiv C-R-C\equiv C-]_n \mathbf{1} (R = aryl)$ spacer group) have been reported.4 The dialkynyl ligands, and related but neutral diisocyanide ligands, are particularly well suited to the design of rigid-rod polymers and examples are now known with Pt-Pt bonds and even Pt3 cluster units in the backbone as illustrated by 2 and 3, $PP = Ph_2PCH_2PPh_2$.^{5,6} The first part of this article will describe the further development of this field to include gold-containing rigid-rod polymers.



Gold-containing oligomers and polymers

Gold(I) tends to have a coordination number of two with linear stereochemistry,³ so it is well suited to form linear rigid-rod polymers. If neutral polymers are to be formed, one neutral ligand L and one anionic ligand X⁻ are required for each gold(I) centre. Suitable ligands might then include L–R–X⁻, where R is a linear spacer group, and L might be an isocyanide and X⁻ an acetylide. Alternatively, one ligand L–R–L and -X–R–X⁻ could be used for each two gold(I) centres. The general types of polymers targetted are then shown as **4–6**. Since many of these polymers proved to be insoluble, it has been important to prepare model compounds containing only two gold(I) atoms, by using capping monodentate ligands in combination with one

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bridging ligand, in order to optimise the synthetic methods and to facilitate characterization of the polymers.

 $\begin{array}{c}
-\left[L-L-Au-X-X-Au \right]_{n} \\
4 \\
-\left[L-X-Au-L-X-Au \right]_{n} \\
5 \\
-\left[L-X-Au-X-L-Au \right]_{n} \\
6 \\
\end{array}$

Diisocyanides, diacetylides and isocyanoacetylides

Since the isocyanide functionality is sensitive to bases, the most successful synthetic route to isocyanide(alkynyl)gold(1) complexes is by reaction of oligomeric or polymeric compounds (AuC=CR)_n, in which the alkynyl ligand bridges by bonding to one gold atom through the σ donor and to a second gold atom using its π electrons,⁷ with an isocyanide ligand. Although the explosive Au₂C₂ has been known for many years, the more stable (CAUTION: but still potentially explosive) digold diacetylides (AuC=C-Ar-C=CAu)_n 7 needed for this work were unknown and were prepared according to eqn. (1), B = base, in which the aryl spacer group Ar = 1,4-C₆H₄, 4,4'-C₆H₄C₆H₄ or 1,4-(2,5-Me₂C₆H₂).⁸

 $2[Me_2SAuCI] + HCC-Ar-CCH + 2 B$ \downarrow $2 Me_2S + 2 BH^+CI^- + {Au-C=C-Ar-C=C-Au}_n (1)$

Suitable binuclear gold(I) model compounds [RN=CAuC=C-Ar-C=CAuC=NR] **8** (R = Bu^t or Xy = 2,6-dimethylphenyl) and [RC=CAuC=N-Ar-N=CAuC=CR] **9** [R = Bu^t or Ph, Ar = 1,4-C₆H₄, 1,4-(2-MeC₆H₃), 1,4-(2,6-Bu^t₂C₆H₂), 1,4-(C₆Me₄), 1,4'-(2,6-Me₂C₆H₂)₂], were then prepared as shown in eqns. (2) and (3).⁸

$$\frac{1}{n} \{AuCC-Ar-CCAu\}_{n} + 2 RNC \rightarrow [RN=C-Au-C=C-Ar-C=C-Au-C=NR] (2) \\ 8 \\ \frac{2}{n} \{AuCCR\}_{n} + CN-Ar'-NC \rightarrow [RC=C-Au-C=N-Ar'-N=C-Au-C=CR] \\ 9 \end{cases}$$
(3)

While eqns. (2) and (3) indicate that the products are molecular in nature, and this is the case in solution, the compounds associate in the solid state either through π stacking between aryl groups of neighbouring molecules⁹ or, more commonly, through intermolecular Au…Au bonding.⁸ These weak Au…Au interactions, which are known in several other classes of gold(I) complexes, are thought to have strengths of 5–10 kcal mol⁻¹, similar to the strength of hydrogen bonds, and are thought to arise from relativistic London forces.¹⁰ The association present in crystals of [PhC=C-Au-C=NBut₂C₆H₂N=C-Au-C=CPh] comprises both aryl π stacking and Au…Au bonding and is shown in Fig. 1.

It was then possible to prepare polymers **10** containing alternating diacetylide and diisocyanide ligands according to

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Fig. 1 The intermolecular association present in the solid state structure of [PhC=CAuC=NBu^t₂C₆H₂N=CAuC=CPh] due to (*a*) π -stacking and (*b*) Au···Au bonding. The Au···Au distance is 3.174(1) Å.

eqn. (4) (Ar and Ar' are as defined earlier). The polymers are

$$1/n \{AuCC-Ar-CCAu\}_n + CN-Ar'-NC$$

$$\downarrow$$

$$\{-Au-C=C-Ar-C=C-Au-C=N-Ar'-N=C-_n\}$$

$$10$$

$$(4)$$

insoluble, which might have been predicted since intermolecular association through π stacking and/or Au…Au bonding will lead to effective crosslinking of the linear rigid-rods into a three-dimensional network. Though each individual interaction is likely to be weak, the combination of many interactions for each polymer chain is likely to give strong crosslinking leading to insolubility. The polymers are therefore characterised only in the solid state by elemental analysis and by comparison of spectroscopic data with those of the well characterised model compounds.⁸

One interesting property of these gold(I) complexes is that they are emissive at room temperature either in the solid state or in solution.^{9,11} The emission is strongly red shifted in the solid compared to solution state as illustrated in Fig. 2, particularly



Fig. 2 The emission spectra of XyNC–Au–CCC₆H₄NO₂-4, (*a*) in solution in CH₂Cl₂ and (*b*) in the solid state, showing the red shift in the solid state. In this case the association in the solid state is due to π -stacking.

when Au…Au bonding or π stacking is present in the solid state structures. In addition, there is a red shift in the emission and a decrease in emission intensity as the molecules increase in size, as illustrated for the solid state spectra shown in Fig. 3, and this



Fig. 3 The solidstate emission spectra of gold(1) complexes showing the red shift with increasing molecular size: (a) [Bu^tN=C-Au-C=CPh], (b) XyN=C-Au-CCC₆H₄-C₆H₄CC-Au-C=NXy] and (c) {Au-C=C-C₆H₂Me₂C=C-Au-C=NC₆H₂Bu^t₂)N=C}_n

provides evidence for at least some π conjugation in the rigidrod chains.⁹

The new ligands $4\text{-HC}\equiv\text{CC}_6\text{H}_4\text{N}\equiv\text{C}$ and $4\text{-HC}\equiv\text{C}_-2\text{-MeC}_6\text{H}_3\text{N}\equiv\text{C}$ bind readily to gold(1) in forming the complexes

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such as $[4\text{-HC}\equiv\text{CC}_6\text{H}_4\text{N}\equiv\text{C}-\text{Au}-\text{Cl}]$ **11** and $[4\text{-HC}\equiv\text{C}-2\text{-MeC}_6\text{H}_3\text{N}\equiv\text{C}-\text{Au}-\text{C}\equiv\text{CBu}^t]$ **12**. The acetylide derivatives such as **12** give weak Au···Au bonded association in the solid state [Au···Au 3.479(2) Å] and form oligometric complexes H-(C=C-Ar-N=C-Au-)_n-C=CBu^t **13** by elimination of Bu^tCCH on heating as illustrated in Scheme 1.¹² The oligometric tend to precipitate from solution when n = 4-6 and then no further chain growth occurs.



Diphosphines, diacetylides and phosphinoacetylides

Diphosphines cannot give strictly linear rigid-rod compounds since there will be a tetrahedral angle at each phosphorus atom. The question then arises as to whether these ligands will give polymers at all, since ring formation is also possible.

The digold(1) diacetylides described above can be capped with monodentate phosphine ligands such as PMe₃ to give binuclear model complexes such as $[(Me_3P)Au-C\equiv C-C_6H_2Me_2-C\equiv C-Au(PMe_3)]$ **14** and this forms loose polymers in the solid state by intermolecular Au···Au bonding (Fig. 4).^{9,13}



Fig. 4 The intermolecular association through Au--Au bonding in the complex [(Me_3P)Au-C=C-C_6H_2Me_2-C=C-Au(PMe_3)]

The diphosphines $Ph_2PC_6H_4PPh_2$ or $Pr^i_2PC_6H_4C_6H_4PPr^i_2$ can also give binuclear model complexes such as $PhC\equiv C-Au$ - $Pr^i_2PC_6H_4C_6H_4PPr^i_2-Au-C\equiv CPh$ **15** which has the *anti* conformation with respect to the two P-Au vectors as shown in Fig. 5; the bulky Pr^i groups prevent the formation of



Fig. 5 The anti conformation of the two P–Au vectors in [PhC=C–Au-Pri_2PC_6H_4C_6H_4PPri_2–Au–C=CPh] 15

intermolecular Au···Au bonding in **15**. It is then straightforward to prepare polymers (Au–C=C–Ar–C=C–Au–PR₂–Ar'–PR₂–)_n **16** incorporating both diphosphine and diacetylide bridges. It is likely that the *anti* conformation of the P–Au vectors in **15** is

maintained in these polymers, which are sufficiently soluble when $R = Pr^i$ to allow molecular mass determination by GPC. The improved solubility probably arises because the bulky Pr^i groups prevent crosslinking by intermolecular Au…Au bonding.

It is possible to tailor the system to give rings instead of polymers. Thus, ligands $R_2PCH_2PR_2$ give digold complexes in which the *syn* conformation of the two P–Au vectors is preferred so as to allow intramolecular Au…Au bonding, as for example in CH₂(PCy₂–Au–O₂CCF₃)₂ **17** or CH₂(PPh₂–Au–C=CBu^t)₂ **18** shown in Fig. 6.^{14,15} This conformation is



Fig. 6 The syn conformation of the two P–Au vectors in $[CH_2(PCy_2-Au-O_2CCF_3)_2]$ 17 and $[CH_2(PPh_2-Au-C\equiv CBu^t)_2]$ 18

maintained on reaction of **17** with rigid-rod bridging ligands and so large rings are formed in [CH₂(PR₂–Au–C≡C–Ar–C≡C–Au–PR₂)₂CH₂] **19** or [CH₂(PR₂–Au–C≡N–Ar–N≡C–Au–PR₂)₂CH₂]⁴⁺ **20**. The structure of the complex **20** with R = cyclohexyl and the bridging ligand 1,4-C≡NC₆H₄N≡C is shown in Fig. 7.



Fig. 7 The structure of the cationic ring complex 20 (R = Cy and Ar = 1,4-C_6H_4)

It is also possible to use mixed phosphine–acetylide donors in forming polymers of gold(1). Thus the ligands $Ph_2PC\equiv CH$ and $Pr_2PC\equiv CH$ form model complexes $HC\equiv CPR_2$ –Au–Cl which, on treatment with base, can eliminate HCl to give the polymers $\{R_2PC\equiv C-Au-\}_n 21$.¹⁶

Angular diacetylides and triacetylides

In the complexes with diphosphines or phosphinoacetylides, the chains are not strictly linear because of the tetrahedral angle at phosphorus, yet polymers can still be formed in preference to the alternative ring structures. What will happen if an angle is introduced in the diacetylide bridge? The dialkyne 1,3-(HC=C)₂C₆H₃Me-5 yields digold(I) model complexes 1,3-(L-Au-C=C)₂C₆H₃Me-5 **22** (L = phosphine, phosphite or isocyanide ligand) which form ribbon structures in the solid state through Au…Au bonding as seen in Fig. 8.¹⁷



Fig. 8 The intermolecular association through Au…Au bonding in the complex [1,3-(L–Au–C=C)₂C₆H₃Me-5] [L = P(OMe)₃]

Kinked polymers such as 23 are formed when linear diisocyanide ligands are used but, if the neutral bridging ligand

is also non-linear, then ring structures such as ${\bf 24}$ are formed instead (Scheme 2). 17



Scheme 2 Reagents: i, C₆H₄(CN)₂; ii, Ph₂PCH₂PPh₂

If a third acetylide link is added as in 1,3,5-(HC=C)₃C₆H₃, the gold derivatives can in principle form more complex network polymers either through intermolecular Au···Au bonding or through the use of bridging ligands. The capped complexes 1,3,5-(L-Au-C=C)₃C₆H₃ **25** are found to form one-dimensional ribbon structures in the solid state with one gold atom not taking part in Au···Au bonding (Fig. 9). With all bridging ligands,



Fig. 9 The intermolecular association through Au…Au bonding in the complex [1,3,5-(L-Au-C=C)_3C_6H_3] (L = Bu⁴N=C)

whether the strictly linear diisocyanides or angular diphosphines, insoluble polymers **26** are formed (Scheme 3).¹⁸



Scheme 3 Reagents: i, [AuCl(SMe2)], NaOAc; ii, 3L; iii, 1.5 L-L

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Rings and polymers with diphosphine and bis(pyridyl) ligands The principles determining if rings or polymers would be formed were now understood in general terms but the detailed structures of the polymers could not be determined since they could not be crystallised. A series of experiments was carried out next using flexible diphosphine ligands $(CH_2)_n(PPh_2)_2$ and a more labile linear bridging ligand *trans*-1,4-bis(pyridyl)ethene. It was argued that the intramolecular Au-Au bonding interactions would decrease progressively with increasing *n* and so the preferred structure would switch from the large rings to polymers at some point in the series (Scheme 4). Further, the polymers could reversibly cleave to smaller fragments in solution owing the lability of the pyridine donors and this might allow crystallisation and so to full structural characterisation of the polymers.¹⁹



Scheme 4 $X = CF_3CO_2$, $P = PPh_2$

With $(CH_2)_2(PPh_2)_2$, the ring structure $[Au_4(\mu-Ph_2PCH_2CH_2PPh_2)_2(\mu-NC_5H_4CH=CHC_5H_4N)_2]^{4+}$ **27** is preferred as shown in Fig. 10 but the Au…Au distance of 3.625(3) Å indicates very weak Au…Au bonding and no significant Au…Au attraction is expected for higher values of n.¹⁹

The switch to a polymeric structure $[{Au_2[\mu-Ph_2P(CH_2)_nPPh_2](\mu-NC_5H_4CH=CHC_5H_4N)}_n]^{2n+}$ **28** occurs when n = 3 and the polymer **28a** has an interesting sinusoidal conformation as shown in Fig. 11(*a*), since the conformation of adjacent P–Au vectors is *syn*. There is then a switch to the *anti* conformation of P–Au vectors when n = 4, such that a more stretched polymer chain is formed in **28b** [Fig. 11(*b*)].¹⁹

An interesting case occurs when n = 5, since three different structural forms have been crystallised (Fig. 12). Two of these



Fig. 10 The structure of the cationic ring complex $[Au_4(\mu\text{-}Ph_2PCH_2CH_2PPh_2)_2(\mu\text{-}NC_5H_4CH=CHC_5H_4N)_2]^{4_+}$



Fig. 11 The structures of the cationic polymer chains $[{Au_2[\mu-Ph_2P(CH_2)_nPPh_2](\mu-NC_5H_4CH=CHC_5H_4N)}_n]^{2n+}; (a) n = 3; (b) n = 4$



Fig. 12 The structures of the helical (*a*) cationic polymer chains $[{Au_2[\mu-Ph_2P(CH_2)_5PPh_2](\mu-NC_5H_4CH=CHC_5H_4N)}_n]^{2n+}$, and of the cyclobutane ring form (*b*)

are polymers **28c**, one of which has the sinusoidal conformation as in **28a** but the other has a conformation intermediate between *syn* and *anti* and the resulting chain adopts a helical structure [Fig. 12(*a*)]. In most of the structurally characterised polymers, the chains pack parallel to one another but the helical polymer has chains that cross over one another while running in mutually perpendicular directions. The third structural form with n = 5proved to be a novel ring structure with a central cyclobutane ring formed by a 2 + 2 cycloaddition reaction of two bis(pyridyl)ethylene ligands [Fig. 12(*b*)]. Further study showed that this form was only obtained when crystallisation was carried out in the open laboratory and it is thought to be formed by a photochemical cyclisation of small amounts of ring structure present in equilibrium with the chain forms as shown in Scheme $5.^{16}$



Scheme 5 $P = PPh_2$

The complex with n = 6 proved to be a stretched polymer **28d** (Fig. 13) whose structure is similar to that of **28b**, having *anti* conformation of adjacent P–Au vectors but with the long (CH₂)₆ chain partly folded back on itself.¹⁶



Fig. 13 The structure of the cationic polymer chain [{Au₂[μ -Ph₂P(CH₂)₆PPh₂](μ -NC₅H₄CH=CHC₅H₄N)}_{*n*}]²ⁿ⁺

The polymers **28** are not conjugated since there is a saturated carbon chain in the diphosphine ligands. However, conjugated polymers can be prepared by using the diphosphine ligands *trans*-Ph₂PCH=CHPPh₂ or [Fe(η^5 -C₅H₄PPh₂)₂]; the structure of the polymer **29** prepared from the latter ligand is shown in Fig. 14 and has the stretched polymer form with *anti*



Fig. 14 The structure of the cationic polymer chain $[\{Au_2[\mu-Fe(C_5H_4PPh_2)_2](\mu-NC_5H_4CH=CHC_5H_4N)\}_n]^{2n+}$

conformation of adjacent P–Au vectors. This polymer, as a pressed disc, converts from being an insulator to a semiconductor when doped with iodine, partial oxidation of ferrocene to ferricenium centres is thought to be a likely rationalisation of this observation.¹⁶ In conclusion, it is now possible to tailor the structures of gold(1) compounds with bridging ligands to give either rings or polymers. The polymers have interesting structures and preliminary studies indicate the possibility of optical and electronic properties based on the conjugation along the chains.

Platinum-containing oligomers and polymers

The synthesis of oligomers or polymers with platinum atoms in the backbone is based on the two simple reactions shown in eqns. (5) and (6). The first is a ligand substitution of a diimine



ligand such as 4,4'-di-*tert*-butyl-2,2'-bipyridine onto a dimethylplatinum(II) centre by displacement of weakly bound Me₂S ligands from $[Pt_2Me_4(\mu-SMe_2)_2]$ **30** to give **31**,²⁰ while the second involves oxidative addition of an alkyl halide to the platinum(II) centre of **31**, a reaction which occurs easily for primary alkyl halides and is tolerant to a wide range of functional groups.²¹ Both reactions occur in almost quantitative yield and so are ideal for multistep syntheses as described below.

Linear chain platinum polymers

The oxidative addition to platinum(II) of alkyl halides containing polymerisable substituents can lead to polymers with organoplatinum(IV) substituents as side chains,²² but the key to making polymers with platinum atoms in the backbone is to use alkyl halides with a bipyridine substituent. Thus, the oxidative addition of a bromomethyl derivative of 2,2'-bipyridine, 4-BrCH₂-4'-Me-2,2'-(C₅H₄N)₂ **32**, to **31** gives a platinum(IV) complex with a free bipyridine group, which can then coordinate to a second dimethylplatinum unit, and repetition of the sequence can give oligomers with platinum atoms in the backbone as shown in Scheme 6.²³

A simple self-assembly of a platinum containing polymer occurs on reaction of **32** with **30** as shown in Scheme 7. Displacement of the Me₂S ligands from **30** gives the platinum(II) monomer **33** which undergoes polymerisation by intermolecular oxidative addition.²³

Dendrimeric platinum polymers

To make a dendrimer, it is necessary to introduce a branch in each generational growth step.²⁴ This requires at least a trifunctional reagent having two alkyl halide and one bipyridine or one alkyl halide and two bipyridine units as present in **34** and **35** respectively. The first successful synthesis is a convergent



method based on the reagent **34** (Scheme 8). Reagent **34** can add to 2 equiv. of **31** to give the diplatinum(IV) complex **36**, which







Scheme 7

can then add a dimethylplatinum(II) group to the free bipyridine to regenerate a reactive platinum(II) centre in 37, whose structure is shown in Fig. 15.25

Now repetition of the cycle using 37 and 34 gives a Pt₇ dendrimer 38 (Scheme 9). One more generation can be grown, but the reactive platinum(II) centre, which is formed at the centre of the molecule in a convergent synthesis, becomes increasingly sterically congested with each generation and eventually the oxidative addition step fails.²⁵

The self-assembly of a hyperbranched polymer with platinum atoms in the backbone is readily achieved by reaction of 34 with **30**. The first step is ligand substitution to give the platinum(II) complex, which then undergoes polymerisation by intermolecular oxidative addition (Scheme 10).25

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Scheme 8



Fig. 15 The structure of the Pt^{IV}₂Pt^{II} complex 37



A divergent method for dendrimer growth is based on the reagent 35, which contains one bromomethyl group and two bipyridine groups. With this system, the reactive platinum(II)



centres are formed at the periphery of the dendrimer and it is easy to introduce a different metal in the outer generation as shown in Scheme 11, using as a source of dimethylpalladium units the complex $[Pd_2Me_4(\mu-pyridazine)_2]$ **39**.²⁶



Scheme 11

Stars and exotic molecules based on polyfunctional cores Polyfunctional cores are useful for facilitating the rapid growth of complex molecules. Two useful core molecules for platinum oligomers are **40** and **41**. The synthesis of a Pt₉ dendrimer by





use of the core reagent 40 and the dendrimer reagent 34 is shown in Scheme $12.^{26}$

The core reagent **41** is useful for assembling four molecules which contain one platinum(II) centre each, including simple molecules like **31** or the more complex linear or dendrimeric molecules prepared in Schemes 6, 8 and $9.^{23,25,27}$ An example is shown in Scheme 13 and the most complex example so far prepared is the Pt₂₈ dendrimer shown in Fig. 16 and formed by coupling four Pt₇ dendrimer units **38** to the tetrafunctional core.



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Fig. 16 Proposed structure of the Pt₂₈ dendrimer

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Notes and References

- 1 J. R. Ferraro and J. M. Williams, in *Introduction to Synthetic Electrical Conductors*, Academic Press, New York, 1987, p. 139.
- 2 R. J. H. Clark, in *Lower-Demensional Systems and Molecular Electronics*, ed. R. M. Metzger, P. Day and G. C. Papavassilion, Plenum, New York, 1991, p. 263.
- R. J. Puddephatt, *The Chemistry of Gold*, Elsevier, Amsterdam, 1978.
 (a) J. Lewis, M. S. Khan, A. K. Kakkar, B. F. G. Johnson, T. B. Marder, H. B. Fyfe, F. Wittman, R. H. Friend and A. E. Dray, *J. Organomet.*
- Chem., 1992, 425, 165; (b) S. J. Davies, B. F. G. Johnson, M. S. Khan and J. Lewis, J. Chem. Soc., Chem. Commun., 1991, 187.
 5 M. J. Irwin, G. Jia, J. J. Vittal and R. J. Puddephatt, Organometallics,
- 5 M. J. Hwin, G. Jia, J. J. Vittal and R. J. Puddepnatt, Organometallics, 1996, **15**, 5321.
- 6 A. M. Bradford, E. Kristof, M. Rashidi, D.-S. Yang, N. C. Payne and R. J. Puddephatt, *Inorg. Chem.*, 1994, **33**, 2355.
- 7 D. M. P. Mingos, J. Yau, S. Menzer and D. J. Williams, Angew. Chem., Int. Ed. Engl., 1995, 34, 1894.
- 8 M. J. Irwin, G. Jia, N. C. Payne and R. J. Puddephatt, Organometallics, 1996, 15, 51.
- 9 M. J. Irwin, J. J. Vittal and R. J. Puddephatt, *Organometallics*, 1997, 16, 3541.
- 10 J. Li and P. Pyykko, Chem. Phys. Lett., 1992, 197, 586.
- (a) C.-M. Che, H.-K. Yip, W.-C. Lo and S.-M. Peng, *Polyhedron*, 1994, 13, 887; (b) V. W.-W. Yam and S. W.-K. Choi, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 4227.
- 12 G. Jia, N. C. Payne, J. J. Vittal and R. J. Puddephatt, *Organometallics*, 1993, **12**, 4771.
- 13 G. Jia, R. J. Puddephatt, J. D. Scott and J. J. Vittal, *Organometallics*, 1993, **12**, 3565.
- 14 G. Jia, R. J. Puddephatt and J. J. Vittal, J. Organomet. Chem., 1993, 449, 211.
- 15 N. C. Payne, R. Ramachandran and R. J. Puddephatt, Can. J. Chem., 1995, 73, 6.
- 16 M. J. Irwin, L. M. Rendina, J. J. Vittal and R. J. Puddephatt, *Chem. Commun.*, 1996, 1281; M. J. Irwin, PhD thesis, University of Western Ontario, 1997.
- 17 M.-A. McDonald, H. A. Jenkins and R. J. Puddephatt, unpublished work; M.-A. McDonald, MSc Thesis, University of Western Ontario, Canada, 1997.
- 18 M. J. Irwin, Lj. Manojlovic-Muir, K. W. Muir, R. J. Puddephatt and D. S. Yufit, *Chem. Commun.*, 1997, 219.
- 19 M. J. Irwin, J. J. Vittal, G. P. A. Yap and R. J. Puddephatt, J. Am. Chem. Soc., 1996, 118, 13101.
- 20 J. D. Scott and R. J. Puddephatt, Organometallics, 1983, 2, 1643.
- 21 L. M. Rendina and R. J. Puddephatt, Chem. Rev., 1997, 97, 1735.
- 22 S. Achar, R. J. Puddephatt and J. D. Scott, *Polyhedron*, 1996, **15**, 2363; *Can. J. Chem.*, 1996, **74**, 1983; S. Achar, J. D. Scott, J. J. Vittal and R. J. Puddephatt, *Organometallics*, 1993, **12**, 4592; S. Achar, J. D. Scott and R. J. Puddephatt, *Organometallics*, 1992, **11**, 2325.
- 23 S. Achar and R. J. Puddephatt, Organometallics, 1995, 14, 1681.
- 24 N. Ardoin and D. Astruc, Bull. Soc. Chim. Fr., 1995, 132, 875.
- 25 S. Achar, J. J. Vittal and R. J. Puddephatt, *Organometallics*, 1996, 15, 43; S. Achar and R. J. Puddephatt, *Angew. Chem., Int. Ed. Engl.*, 1994, 33, 847.
- 26 G.-X. Liu and R. J. Puddephatt, Organometallics, 1996, 15, 5257.
- 27 S. Achar and R. J. Puddephatt, J. Chem. Soc., Chem. Commun., 1994,

8/00244D

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