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CYCLOMETALATED COMPLEXES OF 8-METHYLQUINOLINE AND DERIVATIVES WITH THE PLATINUM METALS

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CONTENTS

A. INTRODUCTION

Cyclometalations have acquired relative popularity in recent years, as shown by the numerous reviews [1,2] published on this subject over the past decade. Since Hartwell et al. [3] initially cyclometalated 8-methylquinoline (**1**) with Pd(II) and Pt(II) in 1970, this ligand and its derivatives have been extensively studied in order to determine the mechanism of cyclometalation on saturated substrates. Until then, most cyclometalated complexes involved the formation of C(sp^2)–M σ-bonds, rather than the C(sp^3)–M σ-bonds as formed with ligand **1**. A characteristic of **1** is the possibility of forming chiral organometallics through the introduction of a substituent on the metalated carbon. This feature was put to convenient use by Sokolov et al. [4].

This review will concentrate on the cyclometalation of the 8-alkylquinoline and 8-carbonylquinoline derivatives. If data have been derived from studies not directly involving cyclometalation but nevertheless important to the understanding of this reaction, these data have been included. Section B

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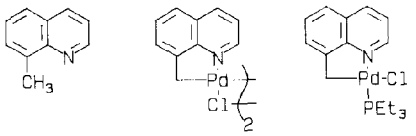
addresses the formation of C(sp^3)–M-bonded complexes as well as some structural studies. Section C covers reactions of these complexes. Section D delineates the formation and chemistry of C(sp^2)–M complexes of **1** prepared by insertion of a platinum metal into either a C–H or a C–C bond (of quinoline 8-carboxaldehyde or 8-ketone respectively).

B. FORMATION OF C(sp^3)-CYCLOMETALATED COMPLEXES

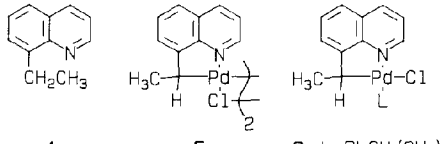
(i) Insertions into C–H bonds

In 1970, Hartwell et al. [3] reported the formation of the chloro-bridged dimer **2** by treatment of 8-methylquinoline (**1**) with lithium tetrachloropalladate(II) in aqueous methanol. Thus complex **2** combines both *N*- and the novel *C*-coordination of **1**. The IR and Raman spectra of these chloro- (and bromo-)bridged dimers have been reported [5]. Upon treatment with $P(Et)_3$, this dimer was easily converted to the corresponding monomer **3**. The ^1H NMR spectrum of **3** showed that the methyl singlet at δ 2.83 had shifted to δ 3.12 ($J_{PH} = 4$ Hz), suggesting a *trans N,P*-orientation. The corresponding platinum complex was prepared and supporting data were to be forthcoming.



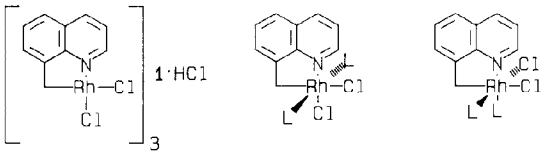
1 2 3

Two years later, realizing the potential of this ligand system in the creation of chiral organometallics, Sokolov et al. [4] used 8-ethylquinoline (**4**) to form cyclometalated complexes **5**–**7** with Pd(II) salts. In order to separate the enantiomeric pair, dimer **5** was cleaved to monomer **6** with optically active 1-phenethylamine; the resulting diastereoisomers were separated and subsequently purified to give a single product **6** ($[\alpha]_D + 29.2°$ (*c* 1.5, CH_2Cl_2)). Metathesis of the amine with $P(C_6H_5)_3$ gave the chiral complex **7** ($[\alpha]_D + 41.5°$ (*c* 4.5, CH_2Cl_2)), whose chirality must arise solely from the presence of the chiral α-carbon, since palladium and its ligands have a planar orientation.



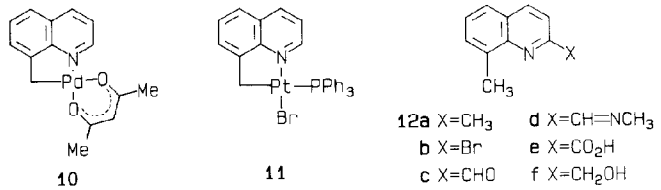
4 5 6 L=PhCH (CH3) NH2
7 L=PPh3

Nonoyama [6,7] extended the metal series by the incorporation of Rh(III) to form complex **8**, which contains one cyclometalated ligand and is apparently trimeric with an associated protonated ligand **1**. The trimeric nature of **8** was deduced from the low coordination number (4) for Rh(III) and its facile cleavage to monomer **9** via the addition of virtually any coordinating solvent. Upon treatment of **8** with dimethyl sulfoxide (DMSO), IR data of the product suggest *S*-coordination, and both chlorine atoms and the two DMSO molecules are mutually *cis*, respectively, as in **9b**. Treatment of **8** with acetonitrile or pyridine generated proposed dimers in which these ligands are *N*-coordinated. However, with tri-*n*-butylphosphine, **9a** is proposed on the basis of a single triplet ($J = 7$ Hz) in NMR for the methylene and IR bands at 318 and 218 cm^{-1}. With both dimethylsulfide and triphenylarsine, the structures $[Rh(Cl_2)(1H)L_2]$ were not delineated.



8 **9a** L=PR_3 **9b** L=DMSO

The use of NMR techniques is extremely helpful in the determination of C–metal bond formation. The use of spectral techniques was extended to include ^{13}C NMR data to verify further the formation of the C–metal bond [8,9]. For complex **10**, *C*-metalation is clearly demonstrated by the downfield shift of the quartet from δ 17.6 to 22.6 (triplet) in its ^{13}C NMR spectrum. The ^{13}C NMR data for **11**, prepared in 85% yield from $Pt(P[C_6H_5]_3)_4$ and 8-(bromomethyl)quinoline, were complex but the methylene resonance was centered at δ 20.5 ($^1J(^{195}Pr–^{13}C) = 741$ Hz; $^2J(^{31}P–^{13}C) = 5.5$ Hz); the *cis* P–C configuration was proposed.



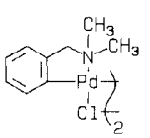
10 **11**

12a X=CH_3 **d** X=CH=NCH_3
b X=Br **e** X=CO_2H
c X=CHO **f** X=CH_2OH

In 1978, Deeming and Rothwell [10] published the first paper discussing the possible mechanism of this reaction. Their results on the cyclopalladation of 2-(substituted)-8-methylquinolines (**12**) with either $[PdCl_4]^{2-}$ or $[Pd(OAc)_2]_3$ in methanol provided interesting insight into the overall process. For **12a–12c**, no cyclopalladation occurred, whereas for **12d–12f** the

desired C–Pd bond was generated even at room temperature. These results strongly indicated that a prerequisite for metalation of the 8-methyl group was its necessity to be in the Pd(II) coordination plane. In the first three cases (**12a–12c**), the quinoline served as a unidentate *N*-donor, in which the methyl group was rotated out of the plane to minimize steric interactions with either the chloride or the acetate. However, with **12d–12f**, bidentate coordination through both the ring nitrogen and either the oxygen or the nitrogen of the 2-substituent was possible. Such coordination initially decreases methyl–metal interactions and permits the methyl group to be further in the plane and thus subject to a strong interaction with the Pd(II), ultimately leading to alkyl palladation.

Shortly after this hypothesis appeared, Deeming et al. [11] added further support for initial *N*-coordination of **1**, prior to C–metal bond formation. Thus, when **1** and **13** were allowed to react, even with a considerable excess of **1**, virtually no reaction occurred under normal conditions, whereas when amine **13** was dissolved neat in **1**, the product **14** was precipitated by addition of ether. Upon dissolution of **14** in $CDCl_3$, **1** dissociated almost completely to regenerate **13**; however, when pyridine, 2-methylpyridine or 7-methylquinoline was added, dimer **13** was readily cleaved. The difficulty in the preparation of the desired complexes was circumvented by replacing the bridging ligand (Cl) with a non-bridging ligand (either ClO_4^- or NO_3^-). When **13** was treated first with AgX ($X = ClO_4^-$ or NO_3^-) and then with **1**, complex **15a** was isolated and its structure supported (NMR), in part, by the chemical shift (δ 5.69) of H_a. The addition of excess **1** did not lead to the formation of **15b**. This is in stark contrast with the reaction of **13** with pyridine, where **15c** was the only product observed. ^1H NMR analysis of **15a** showed an unusual shift of the methyl group from δ 2.83 for free **1** compared with δ 4.07 for **14**, and δ 4.06 ($X = ClO_4$) and δ 4.02 ($X = NO_3$) for **15a** owing to the close H–Pd distance. A similar downfield shift (18.1 to 22.1 ppm) was observed for the methyl carbon in the ^{13}C NMR spectrum of **15a** ($X = NO_3$). This can be attributed to the paramagnetic anisotropy caused by the juxtaposition of the methyl group and the vacant coordination sites of the square-planar d^8-Pd(II) complex. Although the methyl group is closer to the metal center, the rotation barrier is very small since at $-130\,^\circ C$ in $CHFCl_2$ the methyl singlet for **15a** ($X = NO_3$) is only slightly broadened.



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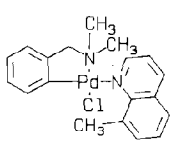

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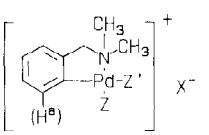


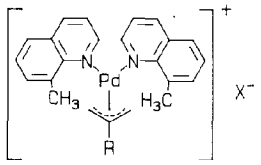
15 $X^- = ClO_4^-$ or NO_3^-

a Z=1; Z'=H_2O

b Z=Z'=1

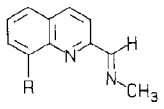
c Z=Z'=pyridine

Success was achieved in synthesizing complexes containing two molecules of **1**, as a unidentate ligand, when an η^3-allyl group was used to occupy two coordination sites on Pd(II) [12]. The ^{1}H NMR data for **16** suggest that a dynamic equilibrium exists in which **1**, and not the allyl moiety, was shown to be exchanging by η^3–η^1 interconversion. At 20 °C in CD_2Cl_2, **16a** (X = ClO_4) showed a single set of 8-methyl resonances which resolved into two equal sets (δ 3.09 and 3.40) at −70 °C, supporting a dissociative isomerization process.

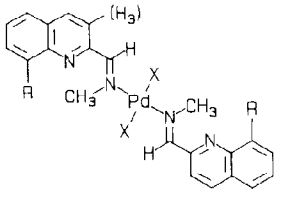


16a R=H
b R=Me

After compiling mechanistic insight into this metalation, Deeming extended his study to include the 8-ethyl (**17a**) and 8-isopropyl (**17b**) derivatives of **12d** [13], which are capable of acting also as *N*-unidentates through the imine nitrogen; bis complexes (**18**) were isolated when the ligands were treated with $PdCl_2$. This mode of coordination of **18** (X = Cl) was presumed to be structurally similiar to that of **18** (X = OAc) in which there was no observed change in the chemical shift of the 8α-C*H* proton and a downfield shift (ca. 3 ppm) of the quinoline *H*-3 signal. Bidentate coordination was,

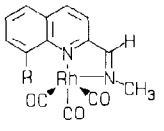


17a R=CH_2CH_3
b R=$CH(CH_3)_2$

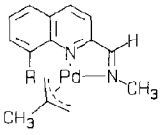


18a R=CH_3
b R=CH_2CH_3
c R=$CH(CH_3)_2$

however, achieved with both Rh(I) (**19**) and Pd(II) (**20**); complexes **19** are five-coordinate, as shown for **19a** by the downfield ($\Delta\delta$ 2.1) shift to 19.9 for the 8-methyl carbon. The small upfield shift (0.02 ppm) for *H-3*, compared with the large downfield shift (2.48 ppm) in **18a**, further supported this mode of coordination. Comparable data were collected for complexes **19b** and **19c**.



19a R=CH_3
b R=CH_2CH_3
c R=CH $(CH_3)_2$



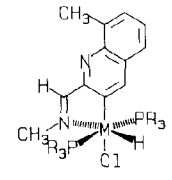
20a R=CH_3
b R=CH_2CH_3
c R=CH $(CH_3)_2$

Similar complexes were formed [13] from **11d**, **17a** and **17b** with $[Pd(\eta^3\text{-allyl})Cl]_2$ in the presence of AgX (X = ClO_4 or BF_4). For Pd(II) complexes **20**, it was anticipated that the steric bulk of the 8-substituents would either prevent bidentate coordination or force the η^3-allyl group to adopt an η^1-coordination. The ^1H NMR spectra of these complexes indicated that neither was the case. This type of coordination showed an interesting temperature dependence (^1H NMR) in that both the η^3-allyl group and ligand are in dynamic equilibrium, in which the terminal carbon atoms of the allyl are equivalent at 20 °C but resolve at −80 °C. The ligand also interchanged *N*-coordination sites, presumably through an unobserved unidentate complex, as shown by the coalescence of the methyl groups of **20c** at 20 °C, with peak resolution occurring at −80 °C. The combined effect of these two processes was a time-averaged plane of symmetry at 20 °C. As determined from models of **20**, distortions must be occurring about the coordination sphere to allow the bidentate mode of coordination. This was demonstrated [13] in the crystal structure of **20c**, where the quinoline moiety is severely distorted and the Pd atom is 1.09 Å out of the plane of the pyridine ring. Despite this distortion a Pd–H contact distance of 2.44 Å was observed.

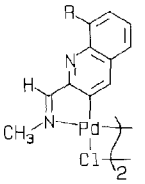
For Pd(II), Rh(I) and Ir(I), quinoline *C(3)*-metalation was observed, whereas the anticipated *C(8)*-metalation occurred only for Pd(II). Oxidative addition of **12d** to $[MCl(C_8H_{14})_2]_2$ (M = Rh or Ir) led to the formation of hydrido complexes **21** in the presence of $P(C_6H_{11})_3$. Confirmation of these structural assignments was readily obtained by NMR; the *H-3* disappeared, *H-4* became a singlet and shifted upfield ($\Delta\delta$ 0.07–0.17) and *C(3)*–M shifted downfield ($\Delta\delta$ 41.8 and 21.0) respectively.

To prepare Pd(II) complex **22a**, Na_2PdCl_4 in refluxing methanol had to be used, which led to a mixture of **22a** and **23a**, whereas use of $[Pd(OAc)_2]_3$ yielded **23b** exclusively. Ligands **17** with most Pd(II) sources afforded complexes **22b** and **22c**, which are believed to be chloro-bridged dimers owing to their poor solubility and generation of monomeric complexes **24** upon treatment with ligands such as pyridine or phosphines. The shift of the *C*–Pd signal (28.9 ppm) in **24a** places it between those for Rh(I) and Ir(I) complexes **21**, as expected. Complex **23b**, formed from $[Pd(OAc)_2]_3$, is

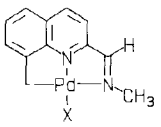
believed to have initially an H_2O molecule coordinated to Pd(II), in addition to **11d** serving as a tridentate ligand. Treatment of **23b** with Cl^- and $P(CH_2CH_3)_3$ gave **25**, in which the imine nitrogen was displaced by the phosphine. When complex **23a** was treated with $P(CH_2CH_3)_3$, **25** was also formed. The ^1H NMR spectrum of **25** confirmed *C(8)*-metalation by the downfield shift of the methylene protons to δ 3.16 from δ 2.81 (for **11d**) as well as the obvious ^{31}P coupling (J_{PH} = 2.9 Hz).



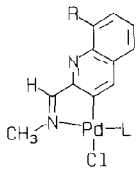
21a M=Rh, R=C_6H_{11}
b M=Ir, R=C_6H_{11}



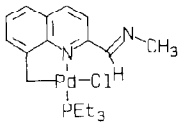
22a R=CH_3
b R=CH_2CH_3
c R=$CH(CH_3)_2$



23a X=Cl
b X=OAc



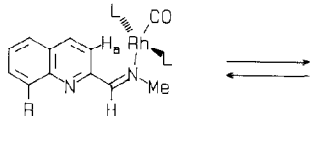
24 L=py or PR'$_3$
a R=CH_3
b R=CH_2CH_3



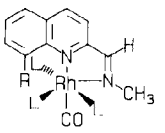
25

The Rh(I) complexes (**26** and **27**) obtained from [Rh(CO)(L')S][ClO_4] (L' = phosphine or arsine; S = acetone) and ligands **12a**, **12d** and **17**, were later studied [14] in detail by Deeming and Rothwell, who found that the shift of the IR stretching frequency of the CO was a good indicator as to whether unidentate or bidentate coordination was achieved. When coordination was unidentate, $\Delta(\nu(CO))$ was small and positive (from 4 to +6 cm^{-1}), while bidentate coordination lead to a larger negative shift (from −12 to −21 cm^{-1}). The equilibrium between **26** and **27** depended on two steric requirements: increased size of the 8-alkyl substituent favors **26**, whereas **27** was favored when $AsP(C_6H_5)_3$ and $PMe_2(C_6H_5)$ were used.

An attempt was made to circumvent the difficulties in obtaining 8α-alkyl-cyclometalated products encountered with the 2-imino derivatives **12d** and **17** by substituting a bis(*tert*-butyl)phosphine group for the imino nitrogen [15] in order to favor formation of bidentate complexes. When **28a** was treated with Na_2PdCl_4 in methanol in a 2 : 1 ratio, the *trans* complex **29** was obtained, with **28a** acting as a unidentate *P*-ligand. The negligible shift



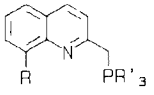
26 R=CH_3, CH_2CH_3, $CH(CH_3)_2$
L=PPh_3, $AsPh_3$, PMe_2Ph,
$P(C_6H_{11})_3$



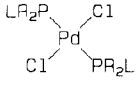
27 R=CH_3, CH_2CH_3, $CH(CH_3)_2$
L=PPh_3, $AsPh_3$, PMe_2Ph,
$P(C_6H_{11})_2$

(^{1}H NMR) of the 8-methyl group (0.01 ppm) and the downfield shift of *H-3* (1.22 ppm) confirmed this orientation. The diminished downfield shift of *H-3* upon coordination, as compared with that in **18a**, is indicative of the increased flexibility of the C–P bond, thus allowing the quinoline rings to distort away from the metal.

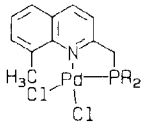
When **28a** and $PdCl_4^{2-}$ were reacted in a 1 : 1 ratio, complex **30** was obtained [15], where **28a** functioned as a bidentate ligand. This orientation was confirmed by the downfield shifts (^{1}H NMR, 1.12 ppm; ^{13}C NMR, 6.1 ppm) of the 8-methyl signals. Another shift characteristic for bidentate coordination of **28a** was that of the CH_2P, which also shifted downfield by 8.7 ppm. This shift of the α-carbon for pyridine-based ligands upon



28 R'=t-Bu
a R=CH_3
b R=CH_2CH_3
c R=$CH(CH_3)_2$



29 R=t-Bu
L=8-methyl-2-quinolinyl

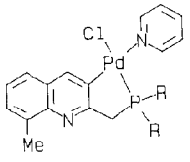


30 R=t-Bu

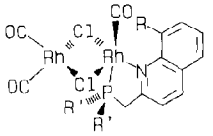
cyclometalation to form five-membered rings has been attributed to ring strain [16]. The structural assignment for **30** was confirmed by X-ray crystallographic analysis [15]. For **28a** to act as a bidentate ligand in a unimolecular Pd(II) complex, severe distortions must occur owing to the juxtaposition of the 8-methyl group and either the Cl or Pd. Three identifiable distortions were noted: rotation about the Pd–N bond (43°) to increase the Me–Cl distance (3.311 Å), a pyramidal distortion about the ring nitrogen, similar to that observed with **20c**, and a buckling of the quinoline ring (ca. 8°). The net effect of these distortions was to cause the normally coplanar Pd–N and methyl–*C(8)* bonds to lie at an angle of 37°.

Reaction of **28a** and **28b** with $[Rh(CO)_2Cl]_2$ led to several characteristic Rh(I) phosphine complexes [15,17–19]. By varying the relative amounts of reactants and the atmosphere (CO or inert), **28a** afforded complexes **31a** and

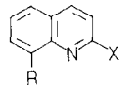
$[Rh(CO)_nCl(L)_m]$ (**32**; $n = 1$ or 2) [15]. Complex **31a** was shown by IR data to be a chloro-bridged dimer in which the P–Rh is five-coordinate, thus forcing the 8-methyl group into close proximity of the Rh atom. The close Me · · · Rh distance was shown by the unusual NMR data for that methyl signal: a triplet ($J = 2.7$ Hz) shifted 0.59 ppm downfield (^{1}H NMR) and a doublet of doublets ($J = 6.7$ and 2.3 Hz) shifted 3.6 ppm upfield (^{13}C NMR). The possibility of *C*-metalation was eliminated as a result of the integration (3H) and the off-resonance decoupling experiments which clearly showed the methyl carbon atom coupled to three protons. It was proposed that these couplings were due to both the ^{103}Rh(I) and ^{31}P nuclei, with a rapid rotation of the methyl group to time-average the coupling over all three protons. With this model, a triplet should be observed when ^1J(Rh–H) $= {}^2J$(P–H); the NMR data were too complex to prove this point. For **31b**, the methylene protons are coupled to nuclei other than the adjacent methyl group; the resolution was insufficient for detailed analysis.



33 R=t-Bu



31a R=CH_3, R'=t-Bu
b R=CH_2CH_3, R'=t-Bu



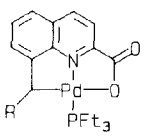
34 R=CH_2CH_3 **35** R=CH $(CH_3)_2$

a X=CH_3 d X=CH=NCH_3
b X=Br e X=CO_2H
c X=CHO f X=CH_2OH

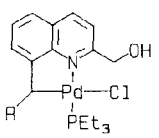
Despite the anticipation that the bulky *P*-substituents in **31** would favor 8-alkyl cyclometalation, the only metalated products obtained with either Pd(II) or Ir(III) were bonded at the quinoline 3-position [15] to afford chloro-bridged dimers similar to **22**. Treatment of this dimer with pyridine gave the very soluble complex **33**. It was noted by these authors that **28a** formed 3-cyclometalated complexes of Ir(III) and Mn(I).

A complete description of the results obtained from the reaction of ligands **12, 34** and **35** with Pd(II) salts was published in 1981 by Deeming and Rothwell [20], updating and expanding the original communications [10]. As previously observed, no cyclometalation occurred with **12a–12c**, **34a–34c** or **35a–35c** under various reaction conditions such as with palladium acetate or $Na_2(PdCl_4)$ at 25 °C in methanol or chloroform, or at 100 °C in acetic acid; however, the remaining ligands (**12d–12f, 34d–34f,** and **35d–35f**) did lead to *C*-metalation with palladium acetate at 25 °C in chloroform. With the 2-imino derivatives **12d, 34d** and **35d**, *C(8α)*-metalation occurred with **12d**, while *C(3)*-metalation was observed with both **34d** and **35d**, as reported previously [10]. With the 2-carboxylates **12e** and **34e**,

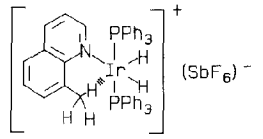
tridentate complexes (**36a** and **36b**) were obtained in which the ligands were coordinated through the ring nitrogen, carboxylate oxygen and 8α-carbon. The initially formed complexes were ill defined and appeared to contain coordinated water; however, metathesis with $P(CH_2CH_3)_3$ led to characterizable complexes. In a similar fashion, **12f** and **34f** led to bidentate complexes **37**, in which the hydroxymethyl group was not *Pd*-coordinated.



36a R=H
b R=CH_3



37a R=H
b R=CH_3



39

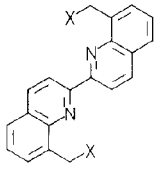
Interesting results were obtained [20] when the relative amounts of reactants (**12d** and PdX_2 (X = Cl, Br, OAc)) and added salts were studied. A 1 : 1 ratio of ligand to Na_2PdCl_4 under reflux in methanol led to a mixture of 3- and 8-metalated products (**22a**:**23a**, 1.4 : 1). Use of $PdCl_2$ with excess LiCl caused metalation to occur solely at the 3-position with the concurrent formation of some non-metalated complex. If the excess halide consisted of a mixture of chloride and bromide ions, the sole product was the non-metalated complex. However, a lower chlorine-palladium ratio (from the original 4 : 1 for Na_2PdCl_4 to 2 : 1 for $PdCl_2[C_6H_5CN]_2$) gave a predominance of the 8-metalated product (8- : 3- = 2.3 : 1), whereas using preformed **18a** in $CHCl_3$ at reflux produced unchanged starting materials. These data suggested that an additional free coordination site is required for *C(8)*- compared with *C(3)*-palladation of **12d**, since excess halide would prevent the freeing of coordination sites and a polar solvent would aid the freeing of sites through solvolysis of the halide ions.

An attempt to answer the questions concerning a detailed trajectory necessary for cyclometalation of the 8α-methyl group of **1** was made by Crabtree et al. [21] with the treatment of **1** with $[IrH_2(S)_2(P\{C_6H_5\}_3)_2]SbF_6$ (S = acetone; **38**). The product, complex **39**, contained a C–H · · · Ir bridge, as determined by crystallographic analysis, which showed that the methyl group was indeed interacting with the Ir(III) (Ir–C, 2.69 Å) and that the Ir–H distance was 2.08 Å. This is in stark contrast to distances corresponding to a bound CH_2–Ir (ca. 2.1 Å) and a non-interacting CH_3–Ir (ca. 3.5 Å). It was claimed [21] that electron density maxima appeared around the methyl carbon in the difference map, corresponding to hydrogen atom positions "reasonable for a methyl group". However, only the position of the interacting hydrogen atom appears to occupy a reasonable position, with the remaining two hydrogen atoms having H–C–H angles significantly

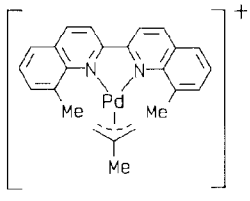
different (146.7° and 93.4°) from the norm. It was not clear from the X-ray data whether this was a real interaction or simply an attempt by the methyl group to orient in the least interactive position. (The two hydrogen atoms facing the iridium were close to being within experimental error of being equidistant from the iridium). An indication of the coordination of **1** was seen in the fact that the methyl group was essentially completely deuterated by **38** in 8 h, with only trace (ca. 5%) deuteration at the quinoline *H-2* position. Other models such as 2- (or 4-) methylquinoline and 2,6-dimethylpyridine gave either trace or no deuterium incorporation.

Additional evidence presented [21] in favor of a significant interaction was an absorption (IR) correlating to a weakened C–H stretch at 2848 cm^{-1}. The ^1H NMR spectrum of **39** revealed that at −20 °C and above, dissociation of **1** occurred. At −80 °C, the methyl group appeared as a singlet at δ 1.11, indicative of rapid exchange of the bridging and terminal protons. Analysis (^1H NMR) of the methyl-d_1 and methyl-d_2 derivatives of **39** showed the presence of an isotopic perturbation effect ($\Delta\delta$ −0.14 and $\Delta\delta$ −0.28 respectively), which requires the methyl group to exist in an environment unsymmetrical enough to produce different hydrogen-to-deuterium ratios at different positions and for these sites to have different chemical shifts. These conditions can only be met if an Ir···H–C interaction occurred.

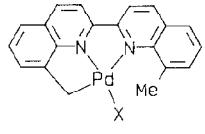
An uncharted yet relevant area of research lies in the chemistry of the related 8,8′-dimethylbiquinoline (**40a**). In 1979, Deeming et al. [22] reported the formation of the Pd(II) complex **41** containing an η^3-allyl group and a ClO_4^- counter-ion. X-ray analysis of **41** showed that the palladium was 1.10 Å out of the plane of the ligand in order to minimize interaction with the methyl groups. The biquinoline rings were very slightly distorted to rotate the methyl groups away from the palladium. In spite of these distortions, the Pd–N distances remained normal (2.125 and 2.126 Å compared with the typical range of 2.0–2.1 Å) [16]. The lack of interactions between the methyl groups and the Pd(II) was shown by the small downfield shift (0.15 ppm) of the CH_3 in the ^1H NMR spectrum of **41**.



40a X=H d X=CN
b X=Li e X=CH $(CO_2CH_3)_2$
c X=Br



41



42a X=OAc
b X=Cl

Recently, Newkome and Evans [23] reported the successful cyclopalladation of **40a**. Reaction of **40a** with $[Pd(OAc)_2]_3$ in anhydrous glacial acetic acid led to the formation of the monometalated complex **42a**. The NMR spectrum of **42a** showed that the CH_2–Pd signal (δ 4.21) shifted downfield (1.29 ppm) (a slightly larger shift than those previously observed [20]), while the non-metalated methyl group shifted only slightly downfield (0.19 ppm), as for **41**. Subsequent dicyclometalation could not be achieved under even the most forcing reaction conditions; this is presumably due to the ring strain associated with the formation of three fused five-membered rings.

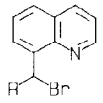
The monometalated complex **42b** was obtained [23] from the reaction of **40b** with Li_2PdCl_4 in tetrahydrofuran (THF) at $-78°C$. Neither of the complexes **42** could be forced to form the second C–Pd bond. This inability to form tandem bonds has been noted [16] with the related 1,10-phenanthroline systems. Additional results found in this study indicated that steric congestion at the binding locus plays a critical role in complex formation, as denoted for **40c–40e**, which failed to form even *N,N*-coordinated complexes with Pd(II) reagents. The increased acidity of the α-alkyl protons of **40d** and **40e** compared with those of **40a** supports Deeming's hypothesis [10] that bidentate coordination is a necessary prerequisite to side-chain metalation in these systems.

(ii) Insertions into C–X bonds

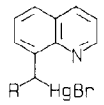
This section addresses the insertion of platinum metals, usually palladium and platinum, into C–X bonds where X = Br, HgBr, SnR_3 or SiR_3. For the organomercurials and organobromides, redox reactions such as Pd(0) or Pt(0) undergoing oxidation to Pd(II) or Pt(II) respectively, were normally observed; for tin and silicon, simple transmetalation was typical.

The first synthesis of this type was reported in 1976 by Sokolov and coworkers [24], where the bromomethyl derivative **43a** was reacted with Pd_2(dibenzylideneacetone)$_3$ to give the bromo analog of **2**, which was then cleaved with $P(C_6H_5)_3$ to give a monomeric complex (**45a**), analogous to **3**. Alternatively, **45** could be prepared directly by the interaction of **43a** and **43b** with $M(0)[P(C_6H_5)_3]_n$ (M = Pd, $n = 4$; M = Pt, $n = 3$). Analogous reactions were run successfully on the 8α-bromoethyl derivative **43b** to give **45d** in 93% yield [24,25]; this was the first example of an M(0) insertion into a secondary C–Br bond. It should be noted that organomercurials, extensively used later by Sokolov [26–31] were also used here, but not with the quinoline-based ligands.

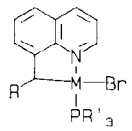
As noted above, Sokolov et al. [4] had successfully utilized the 8-ethylquinoline (4) to synthesize chiral organopalladiums (**5–7**). However, these complexes were initially formed as racemic mixtures, which were subse-



43a R=H
b R=CH_3



44a R=H
b R=CH_3



45a M=Pd (II), R=H, R'=Ph
b M=Pd (II), R=CH_3, R'=Bu
c M=Pt (II), R=H, R'=Ph
d M=Pt (II), R=CH_3, R'=Ph
e M=Ni (II), R=CH_3, R'=Ph
f M=Pd (II), R=CH_3, R'=Ph

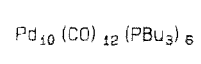
quently resolved [4,32]. Sokolov et al. [26] circumvented this extra step by synthesizing chiral organomercurial **44b** which was readily resolved. Reaction of optically active **44b** with Pd(0)[$P(C_6H_5)_3$]$_4$ in benzene rapidly led to the elimination of Hg(0) and generated the optically active **45f** in 79% yield, with inversion of configuration [26]. Use of Pd_2(dibenzylideneacetone)$_3$ in place of the phosphine complex gave the optically active dimer, which was transformed by treatment with $P(C_6H_5)_3$ to give **45f** without loss of optical activity.

In 1984, Sokolov and coworkers [28,33] presented a detailed study of the reaction of Pd(0) and Pt(0) complexes with bromomercurimethyl and bromomercuriethyl derivatives **44**. Treatment of **44a** with Pt[$P(C_6H_5)_3$]$_3$ gave the cyclometalated complex **45c** in addition to some [$(C_6H_5)_3P)_2$]$PtBr_2$, whereas **44b** led to exclusive formation of this Pt(II) salt. ^{1}H NMR analysis of **45b** showed that the methine proton occurs at δ 3.12 and the methyl protons at δ 1.01. A comparison of complexes **45a** and **45c** showed that the methylene signal for the Pt(II) complex shifted upfield (0.26 ppm).

The geometric structure of **45a** was determined by X-ray crystallography as a benzene solvate [28,29,34]. The palladium coordination sphere consisted of the C(8α) and nitrogen of quinoline; the P–N orientation was *trans* and possessed a slight tetrahedral distortion. The Pd–C, Pd–N and Pd–P distances (mean values) are 2.04 Å, 2.09 Å and 2.26 Å respectively [29] and are typical for these bond types. The Pd–Br bond was longer than expected (2.56 Å compared with 2.45 Å [35]) owing to the strong *trans* effect of a C(sp^3)–Pd σ-bond.

In a variation on the above redox demercuration, Pd(0) cluster **46** was allowed to react with **44b** [30] in benzene to give two palladium-containing compounds, one of which was the monomeric complex **47**. No evidence for CO insertion was detected; the increased stability of the five-membered ring was the rationale.

In 1983, Sokolov and coworkers [31] were successfully able to incorporate Ni(II) using redox demercuration methodology with zero-valent complexes



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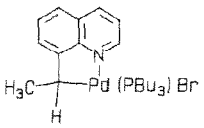
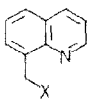


47



48a X=Si $(CH_3)_3$
b X=Sn $(CH_3)_3$

of nickel. Thus treatment of **44b** with $Ni[P(C_6H_5)_3]_4$ gave the red-brown crystalline **45e** which is stable in an argon atmosphere. The ^1H NMR spectrum of **45e** showed the quintet for the methine proton at δ 2.22 and the doublet for the methyl protons at δ 1.12, which are shifted -0.90 ppm and $+0.11$ ppm respectively relative to **45b**.

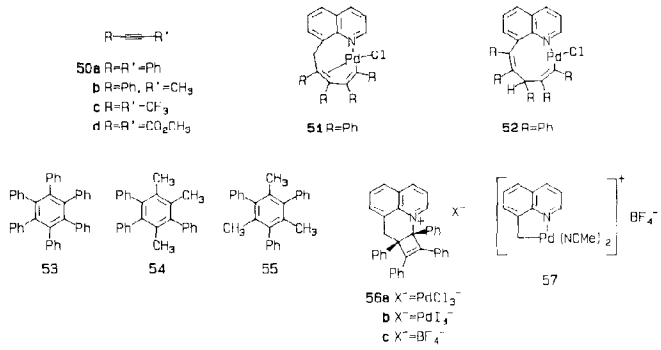
A related transmetalation leading to the formation of C(sp^3)–Pd(II) bonds was recently reported by Suggs and Lee [36]. In this study, the trimethylsilyl (**48a**) and trimethylstannyl (**48b**) derivatives of **1** were synthesized and reacted with the benzonitrile complex $[PdCl_2(C_6H_5CN)_2]$ (**49**) in chloroform. These reactions led to the initial formation of dimer **2**, which was then cleaved in the usual way with $P(C_6H_5)_3$ to give **3** in 10% yield. Significant differences in reactivity were noted: **48b** reacted upon mixing at 25°C, while **48a** reacted only after prolonged reflux.

C. REACTIONS OF C(sp^3)–METAL σ-BONDS

This section presents the reactions of the C–M σ-bond as well as of the complex as a whole, which usually involve cleavage of a chloro-bridged dimer to give new metallocycles.

The lability of the C–M σ-bond is a well-documented feature that is the pivotal reason for such extensive studies of cyclometalated complexes as synthetic intermediates [1]. The use of "activated" unsaturated compounds as reactants for these studies has been common. In 1979, Dehand and coworkers [37] published the first study of the insertion of "activated" alkynes **50a–50c** with dimer **2**. With **50a**, two products were isolated; the first, in poor yield, was the bis insertion product **51** which was characterized (^1H NMR) by the presence of the four-line AB pattern (δ 3.98 (d) and δ 4.16 (d), $J_{H-H} = 15$ Hz) for the methylene protons. The second and major product (25% yield) was hexaphenylbenzene (52). It was observed that the yield of **51** was time dependent, suggesting that it was an intermediate for **53**. This suggestion has recently been shown to be unlikely [38] and the presence of **53** may have been "due to the presence of impurities in the starting complex **2**" [38].

The reaction of **2** with diphenylacetylene (**50a**) in refluxing chlorobenzene (boiling point, 132°C) was recently shown [38,39] to afford **51** in 80% yield.

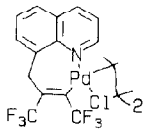


This mediocycle upon prolonged (ca. 3 h) refluxing in chlorobenzene generated isomer **52** as the major product, as shown by the disappearance of the CH_2 moiety (two doublets at δ 3.90 and 4.16) and the appearance of two singlets at δ 6.40 and 6.47, in support of isomer **52**. A second product was isolated in low yield and shown to be the red crystalline tetraphenylcyclobutene adduct **56a** which was derived from **51**. The NMR data and X-ray diffraction study established the structure of **56a**.

The use of the iodide dimer of **2** enhanced the reactivity and yield of the product; the purple crystalline **56b** was isolated in quantitative yield (based on iodine) when the reaction was conducted in refluxing toluene. Treatment of the related cyclopalladated derivatives **57** [40] afforded **56c** in quantitative yield [38].

When the unsymmetrical alkyne **50b** was used, a complex mixture was obtained. Although no pure metallocyclic intermediates corresponding to **51** were isolated, their presence was suggested on the basis of the isolation and characterization (^{1}H NMR) of a mixture (7 : 3) of **54** and **55**. All attempts to isolate a monoinsertion intermediate or product with alkynes **50a** and **50b** failed [37].

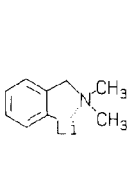
In contrast to these results, when **50c** was used, a monoinsertion product **58** was obtained in 80% yield, in which the chloro bridge remained intact [37]. Further reaction of **58** with either excess **50c** or added **50a** was unsuccessful.



58

In the seventh paper in the series on the cleavage of dimer **2** to produce new cyclometalated complexes, Arlen et al. [41] reported that **2** with lithio

species **59** and **60** gave the biscyclometalated complexes **61** and **62** respectively. Reaction of **2** with lithio *o*-(*N*,*N*-dimethylamino)toluene, however, led to decomposition products only; the analogous bicyclic compounds were not isolated. The *cis* configurations of both **61** and **62** were based on a comparison of the ^{1}H and ^{13}C NMR data with that of the methoxynaphthalene analog **63**, whose X-ray analysis confirmed the proposed [41] more stable *cis* configuration [42].



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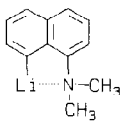

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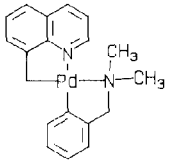
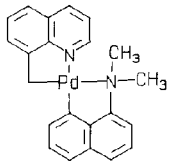


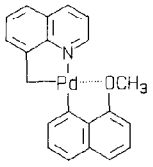
61



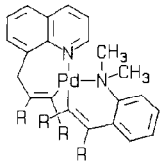
62

Reaction of **61** with **50c** led to the formation of two initial products, one of which disappeared after 2 days to give **64** as the sole product. Complex **64** contains two seven-membered rings resulting from a bis insertion of **50c**, one per C–Pd bond. The X-ray analysis of **64** definitively confirmed the *cis* *Pd*-coordination sphere and the presence of a palladium core with two seven-membered rings. Identification of the transient product showed it to be the isomeric *trans*-**64**, which is relatively unstable and undergoes facile isomerization to the *cis*-**64** upon standing.

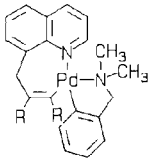
In view of the notable reactivity of **61**, Arlen et al. [41] treated **61** with alkyne **50d**; a mixture of products was obtained from which only **65** has been identified. Elemental analysis of **65** indicated that only one alkyne had been inserted into the Pd–CH_2 bond; this was supported by ^{1}H NMR spectral correlations. These protons appeared as an AB pattern at positions similar to those of **64**, while the benzyl methylene protons were in significantly different positions. Unlike **61**, complex **62** did not form any identifiable cyclometalated complexes.



63

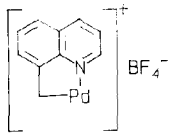


64 R=CF_3



65 R=CO_2CH_3

Recently, when Wu et al. [43] treated the tetrafluoroborate **66** of dimer **2** [3] with 3-hexyne at 25 °C, complex **67** was formed in 20% yield. X-ray crystal data for **67** established its structure.



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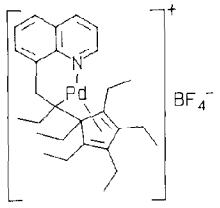

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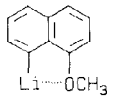


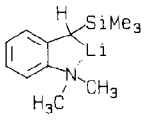
68

Using the same methodology as above, **63** was formed from the lithiated ether **68**, generated from 1-methoxynaphthalene and *n*-butyllithium in ether–hexane, and dimer **2** [42]. X-ray analysis of **63** indicated that the Pd-coordination sphere consisted of a planar molecule with *cis* geometry. The Pd–N distance (2.127 Å) was in the range normally associated with strong *trans* donors, such as phosphines or C(sp^2) bonds. The Pd–O bond was, however, long (2.236 Å) in relation to normal values (2.0–2.1 Å). This could be due to either an inherent weakening of this bond or the stronger *trans* effect of the C(sp^3) (compared with C(sp^2)) σ-bond. Treatment of **63** with phosphine ligands failed to generate any new identifiable organometallic compounds. Insertion of hexafluorobut-2-yne in the Pd–C bond afforded a seven-membered palladocycle, similar to **64**, whose structure was confirmed by X-ray data [44].

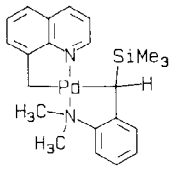
A ligand exchange was reported by Ryabov and Yatsimirsky [45] in which the bound, cyclometalated ligand in **12** was completely replaced by **1** to afford dimer **2** in 64% yield. Even though the possibility existed for a widespread use of this procedure to form novel cyclometalated complexes, no recent examples have been reported.

The inability to form stable metalated complexes containing two benzyl substituents has been ascribed [41] to the softness of this type of ligand. Shortly thereafter, this problem was circumvented by Maassarani et al. [46] who treated **2** with the lithiated trimethylsilyl derivative **69** and obtained in 30% yield [40] the crystalline complex **70**, which with excess alkyne **50c** generated a novel olefin containing a tetrakis(fluoromethyl)-substituted 1,4-dipallado-1,3-butadiene moiety. The facility of this transmetalation reaction was attributed to the stabilizing effect of the $SiMe_3$ group in the organometallic product(s). The structural assignment of **70** was based in part on the ^{13}C NMR data which showed peaks at δ 52.2 and 50.6 for the diastereotopicity of the *N*-methyl groups; δ 20.7 for the *C*H and δ 15.8 for the CH_2Pd.

Over the past 6 years, Braunstein and coworkers [47–49] reported the formation of *O–P*, *C–N* bis complexes via cleavage of the corresponding bromo-bridged dimer of **2**. In their initial paper [47], dimer **2** was treated



69



70

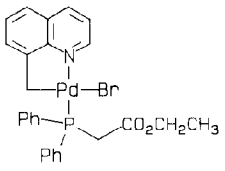
with functionalized phosphine **71a** to give **72**, in which **71a** acted as a simple *P*-coordinated monodentate. Subsequent reaction of **72** (for X-ray data see ref. 48) with $AgPF_6$ gave the cyclometalated complex **73**, whose *trans* P–N orientation was easily confirmed by ^{31}P NMR data.

$(C_6H_5)_2PCH_2Y$

71a $Y=CO_2CH_2CH_3$

b Y=CN

c $Y=CO_2Na$



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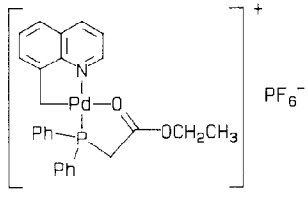


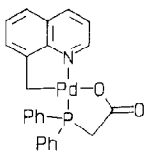
73

Similar phosphine esters have been shown [50] to undergo base-catalyzed dealkylation; thus when **72** was treated with an excess of *n*-butyllithium in THF, the *O*,*P*-chelate **74** was formed [48]. When only one equivalent of **71a** was used, dimer **75** was formed, in which **71a** was a *P*,*C*-bridging ligand. The unsymmetrical nature of **75** was readily apparent in its ^1H NMR spectrum, where the methylene protons on the two different quinoline rings appeared at two distinct chemical shifts (δ 3.00 (d) and 3.11 (d), $J_{H-H} = 14.4$, $J_{H_a-P} = 3.8$, $J_{H_b-P} = 3.4$ Hz; δ 2.95 (d) and 3.23, $J_{H-H} = 14.8$ Hz), with one set appearing as an ABX pattern due to a *P*-coupling.

When **72** was treated with one equivalent of a base (e.g. NaH–THF), complex **76** was formed [47]. This complex was interesting since when it was treated with CO_2(g) a new reversibly generated complex was formed in situ, in which the C*H*–P signal (NMR) disappeared and a signal (δ 13.9) corresponding to an enol appeared. Attempts to isolate this complex failed; however, **77** was presented [47] as a reasonable structural hypothesis.

Complex **76** underwent *C*-alkylation to give a single product **78**, which resulted from the nucleophilic addition of the PC–H bond of the phosphinoketonate to the phenylisocyanate C=O bond [51]. The ^1H NMR data showed a singlet at δ 12.4 for the O···H···N bond, supporting the isomeric assignment.

The successful synthesis of **75**, which contained two different bridging groups, led the Braunstein group [48,52] to investigate further this type of



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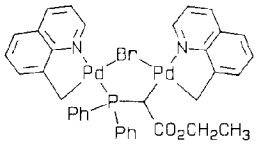
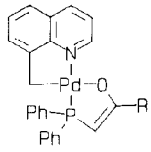
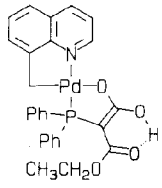


75



76 (R=OCH_2CH_3)
80 (R=Ph)



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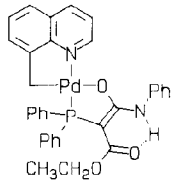
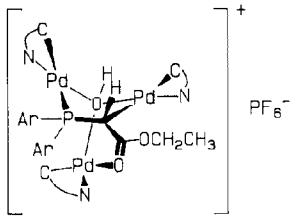


78

complex. Cyclometalated **1** was a useful starting material, since the hard nitrogen and soft C(sp^3) σ-bond allowed considerable control over the site of substitution. When phosphine **71a** was treated with **2** in the presence of $AgPF_6$, a new trinuclear complex **79** was obtained, in addition to the previously observed **75** and **76**. Complex **79** possessed two μ_3-bridges; one was an OH and the other was the anion of **71a**, which was *P*-, *C*-, and *O*-coordinated to three different palladium centers. The structure of **79** was verified by X-ray analysis [48]. This unique complex was presumably formed through the intermediate (Pd–Pd) dimer, which was generated by the abstraction of the bridging halide. This reactive intermediate can then attack unreacted **75** through the ester oxygen, with subsequent cleavage of the bromo analog of **72**, to give an intermediate trinuclear complex lacking the μ_3-OH. The reactivity of this coordinatively unsaturated intermediate then caused an H_2O molecule to form the μ_3-OH bridge. It was suspected [48] that this occurred during purification on silica rather than from the solvent.

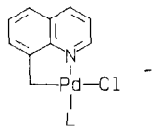


79 N⌒C = 8-methylquinoline

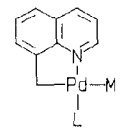
When the related **80** was treated with one equivalent of dichlorophenylphosphine in THF and pyridine, which acts as an HCl trap, facile Pd–N cleavage occurred to give a new air-stable bisphosphino palladium complex. Crystallographic data of this complex confirmed the loss of the initial cyclometalated structure [53].

A related transformation of functionalized phosphine **71c** with **2** was recently reported [48], in which the phosphine contained a free carboxylate rather than ester group. For **71c**, chelation with a cyclometalated Pd(II) complex (for example **2**) would yield neutral complexes such as **74**.

In addition to the reaction of phosphines with dimer **2**, attention has been paid to the formation of Pd–M bonds, where M was a low oxidation state transition metal, e.g. $NaCo(CO)_4$ (**81**), $NaMo(CO)_3(\eta\text{-}C_5H_5)$ (**82**) and $NaKFe(CO)_3NO$ (**83**). Initial studies by Pfeffer et al. [54] showed that **84** could react with metal carbonyl complexes **81** and **82** to give **85**. It appeared that the Pd–M interaction in **85** was ionic, since addition of hexane to the reaction mixture was necessary to precipitate the products. The resultant complex was readily dissociated to starting materials on the addition of NaCl.



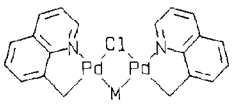
84



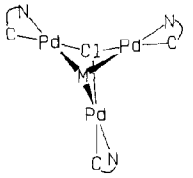
85a L=PPh $(CH_3)_2$, M=Mo $(CO)_3$ (Cp)
b L=PPh $(CH_3)_2$, M=Co $(CO)_4$
c L=4-Mepy, M=Mo $(CO)_3$ (Cp)
d L=py, M=Co $(CO)_4$
e L=py, M=Fe $(CO)_3NO$
f L=CO, M=Mo $(CO)_3$ (Cp)
g L=CO, M=Co $(CO)_4$

In studies directed toward the generation of heteronuclear complexes with two different bridges [55], complex **86b** was prepared from **2** and **81**, in which the $Co(CO)_4$ moiety served as one of the bridging groups. Upon treatment of **86b** with excess **82**, a quantitative yield of **86a** was isolated [48]. Thus displacement reactions of bridging groups is possible. When **86a** was treated with AgX (X = BF_4 or PF_6), the trinuclear complex **87** containing μ_3-Cl and μ_3-Mo bridges was obtained. This was the first example of this type of molybdenum group bridging three non-bonded metal centers.

Despite the apparent stability of these organometallics towards dissociation, Ryabov reported [56–58] the cleavage of the C–Pd bond of **7b** and the related chloro(ligand-*C*,*N*)triarylphosphinepalladium(II) complexes with



85a M=Mo $(CO)_3$(Cp)
b M=Co $(CO)_4$
c M=Fe $(CO)_3NO$



87 N⌒C=8-methylquinoline, M=Mo $(CO)_3$(Cp)

LiCl in acetic acid to generate $PdCl_2[P(C_6H_5)_3]_2$ (**88**) and the free ligand. The formation of the slightly soluble phosphine dimer **88** may, however, be a necessary driving force for this dissociation.

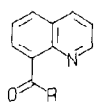
Herring et al. [59] recently reported the treatment of **2** with $[(C_6H_5)_2P]_2C{=}CH_2$ to generate $[CH_2C_{10}H_{16}NPd\{(PPh_2)_2CHCH_2OMe\}]^+ Cl^-$, which with NH_4PF_6 in methanol gave $[CH_2C_{10}H_{16}NPd\{(PPh_2)_2 CHCH_2OMe\}]^+PF_6^-$, as determined from NMR data.

D. FORMATION OF CYCLOMETALATED COMPLEXES CONTAINING $C(sp^2)$–M BONDS AND THEIR REACTIONS

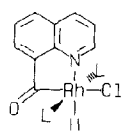
In this section the formation of cyclometalated complexes formed via a $C(sp^2)$ H (or –C) bond cleavage will be discussed. The metals considered are limited to palladium, platinum and rhodium, with the last definitely predominating.

In order to study the mechanism of the Rh(I)-induced decarbonylation of aldehydes, Suggs et al. [60] chose 8-quinolinecarboxaldehyde **89a** as his model substrate, rationalizing that the intermediate will be stabilized via chelation. Thus the treatment of **89** with $RhCl[P(C_6H_5)_3]_3$ (**90**) in CH_2Cl_2 led to the isolation and identification of hydrido complex **91** in 95% yield. Confirmation of the intermediate **91** in the decarbonylation process was accomplished by refluxing a xylene solution of **91** for 4 h from which quinoline, in quantitative yield, as well as *trans*-$RhCl(CO)[P(C_6H_5)_3]_2$ were formed. When **91** was treated with $AgBF_4$ in toluene $-CH_2Cl_2$ at 0 °C, the stable (at 25 °C), hygroscopic, coordinatively unsaturated complex **92** was formed in quantitative yield. Complexes of this type had been thought [61,62] to be intermediates in hydroacylation; treatment of **92** with excess 1-octene and **89a** at 50 °C gave 8-quinolinyl octyl ketone in 55% yield, confirming this premise [60].

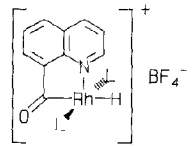
Since insertion of Rh(I) into formyl C–H bonds is a well-known process [63] an interesting mechanistic study of metal insertion into the H–$C(sp^2)$ bond was performed by Suggs and Pearson [64] with 2-pyridyl and 8-



89a R=H
89b R=D

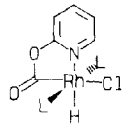


91 L=PPh_3

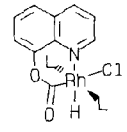


92 L=PPh_3

quinolinyl formates as models. Molecular models indicated that intermediate **93** from 2-pyridyl formate would possess a range of M $\cdots$ H–C angles from 60° to 140° and an M–H distance of 2.4 Å, whereas intermediate **94** from 8-quinolyl formate would have limited M $\cdots$ H–C bond angles from 50° to 90° and a similar M–H bond distance. This difference in allowable angles of attack was necessary for differentiation between the proposed triangular (both formates) and the linear (only pyridyl formate) transition states for metal insertion in a hydrogen bond. Thus both formates cleanly underwent decarbonylation at temperatures slightly above 25°C. In order to eliminate other possible explanations, *N*-coordination was demonstrated to be a prerequisite to decarbonylation, and isotope effects clearly indicated that C–H bond cleavage was the rate-determining step. Thus a triangular interaction was operable in this insertion process. It is interesting to note that Deeming's work [10] on the metalation of **1** indicated a linear interaction.

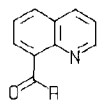


93 L=PPh_3

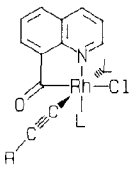


94 L=PPh_3

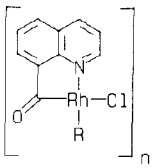
In 1981, Suggs and Cox [65] critically evaluated the reaction of acetylenic ketones **95a** and **95b** with **90** at 40°C for 10 min in CH_2Cl_2. Since the C(sp^2)–C(sp) bond of **95a** and **95b** was known [66] to be reactive towards nucleophiles such as NaOH, the stable *C*-acetylenic complexes **96** were anticipated. The IR and ^{31}P (^1H) NMR data as well as elemental analyses support the acylrhodium(I) acetylide structure. Further confirmation was chemically ascertained by the treatment of **96** with anhydrous HCl in CH_2Cl_2 from which the alkyl (or aryl) acetylene was isolated. However, when styryl ketone **95c** was used, no insertion occurred, but rather **95c** acted as an N,π-bidentate.



95a R=C≡CPh
b R=C≡C(t-Bu)
c R=CH=CHPh
d R=CH_2Ph
e R=CH_2CH_3
f R=CH_3
g R=Bu
h R=CH(CH_3)Ph
i R=C(CH_3)$_2$Ph
j R=Cy
k R=Ph
l R=CH(OCH_3)Ph

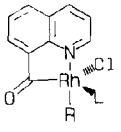


96a R=Ph, L=PPh_3
b R=t-Bu, L=PPh_3

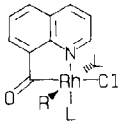


98a R=CH_2Ph
b R=CH_2CH_3
c R=CH_3

In order to study successfully the cleavage of C(sp^2)–C(sp^2) bonds, a more reactive Rh(I) source such as [RhCl(C_2H_4)$_2$]$_2$ (**97**) was used [67], in which the phosphine was replaced by ethylene. Thus, when ketones **95d** and **95f** were treated with **97** in benzene at ambient temperatures, the intermediate chloro-bridged polymers **98** were obtained and subsequently converted to the soluble five-coordinate complexes **99** upon addition of pyridine. Addition of excess pyridine to **99a** gave the six-coordinate complex **100a** whose structure was confirmed by X-ray analysis. The short Rh–acyl bond length (1.949(4) Å) was a unique feature in view of the other Rh(III)–acyl bond lengths which appear in the range 1.97–2.06 Å. Unlike ketones **95a** and **95b**, **95c–95f** do not react with either NaOH or the Rh(I) complex **90**. An η^3-enol complex was generated from **95d** and proven by X-ray crystallographic data [68].



99 L=py
a R=CH_2Ph
b R=CH_2CH_3
c R=CH_3
d R=CH_2CH_2D
e R=*CH(OCH_3)Ph



100 L=py
a R=CH_2Ph
b R=CH_2CH_3
c R=CH_3
d R=CH_2CH_2D
e R=*CH(OCH_3)Ph

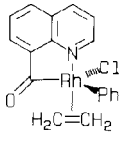
It was previously mentioned that rhodium complexes could be used to conduct hydroacylation reactions. Suggs et al. [69] investigated further aspects of these (*N*,*C*)-quinolinylcarbonyl complexes. When aldehyde **89a** was reacted with Rh(I) complex **97**, the intermediate complex **98b** was formed, in which one of the ethylene groups had been reduced to an ethyl group via addition of the aldehydic proton. Addition of pyridine broke up

polymer **98b** to afford **100b**, as demonstrated by X-ray data. When aldehyde-d_1 **89b** was used, deuterium incorporation occurred exclusively at the terminal carbon, as determined by $^{13}C-D$ coupling data; no scrambling occurred.

When **100b** was treated with the softer *P*-donors, e.g. $P(C_6H_5)_3$, which stabilize Rh(I) complexes, reductive elimination occurred to give ethyl ketone **95e** and $RhCl[P(C_6H_5)_3]_3$ via the five-coordinate monophosphine complex **99b** ($L = P(C_6H_5)_3$). The absence of this elimination without the presence of phosphines could be understood when it was recognized that elimination from **100b** would produce an Rh(I) coordinated to only two quinolines and a chlorine. These donors present insufficient stabilization for the elimination to occur.

An interesting conversion was reported by Suggs and Jun [70] when ketones **95g–95j** were treated with **90** in benzene at 80 °C for 5 h: after the addition of pyridine, the sole product isolated in greater than 90% yield was the ethyl complex **99b**. No evidence for any other alkylrhodium complexes could be found. Formation of **99b** presumably occurred via a β-elimination from the initially formed alkylacyl complex to give an acylrhodium(III) hydride, which was trapped by the bound ethylene. An interesting feature was the Rh(I) insertion into the C–C bond of even **95i**, rather than into a C H bond. This insertion with quinoline ligands is presumably due to the marked preference of this reaction for five-membered intermediates, rather than for six- (or larger-)membered chelates necessary for competing insertion into C–H bonds.

When 8-quinolyl phenyl ketone (**95k**) was reacted [70] with **97**, not only was **99b** isolated but styrene was also formed in 100% yield (1100% based on the catalyst). Insertion occurred into the phenyl–acyl bond to form the intermediate phenylrhodium complex **101**. The phenyl group then added to the terminus of a bound ethylene, as in the above reduction to form a C,π-chelated ethylbenzene complex **102**, which can undergo a β-elimination to give styrene and **95e**. Use of perdeuterated phenyl **95k**-d_5 produced



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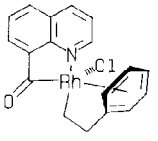
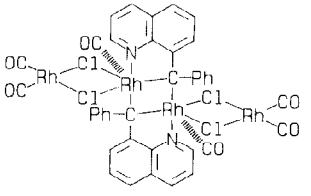


102



104

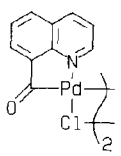
styrene without loss of the ring deuterium label, which excluded the possibility of an intermediate benzyne in the formation of **102**.

Suggs et al. [71] reported that phenyl ketone **95k** with $[RhCl_2(CO)_2]_2$ (**103**) in benzene at 25 °C produced the novel red crystalline tetranuclear dimer **104** in 67% yield with the concurrent evolution of two equivalents of CO_2. The structure of this 1,3-dirhodiacyclobutane **104** was confirmed [68,71] by X-ray analysis.

Suggs and Jun further reported [72] the preparation of the chiral Rh(III) complex **99e** by the reaction of optically active ketone **951** with **97**, followed by the addition of pyridine. Subsequent treatment of **99e** with trimethyl phosphite caused a reductive elimination to occur, regenerating **951** in 71% yield with only a slight loss of optical activity ($[\alpha]_D = -111°$ vs. $-117°$), indicative of dissociation with slow racemization. When **99e** was heated at 90 °C for 1 h, benzaldehyde as well as ethane were formed; thermolysis in CCl_4 afforded CH_3Cl along with benzaldehyde, indicative of a homolysis process. At 60 °C, chiral **99e** underwent facile racemization at the carbon center; rate data were presented.

Despite the extensive studies performed on the quinolinylcarbonyl-rhodium complexes, little is known about the other platinum metals. Anklin and Pregosin reported [73] the reaction of aldehyde **89a** with $PdCl_4^{2-}$ to give the initially formed insoluble chloro-bridged dimer **105**, which with neutral ligands produced the monomeric complexes **106**. The cyclometalation was supported by the absence of the aldehydic proton (δ 11.46) in the ^1H NMR spectrum of **106** as well as by the new position (ca. δ 10.1) for the 2-quinolyl hydrogen.

When the platinum phosphine dimer $[(P\{C_2H_3\}_3)PtCl_2]_2$ (**107**) was used instead of $PdCl_4^{2-}$, Pregosin et al. [74,75] reported the isolation of the *N*-coordinated intermediate **108** in 100% yield on treatment of **89a** with **107**



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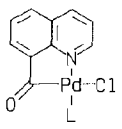
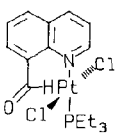


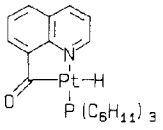
106a L=PPh_3
b L=PEt_3
c L=4-Mepy
d L=$P(C_6H_{11})_3$

at room temperature. Warming a solution of **108** caused insertion into the C–H bond to give the expected complex **106b**. As previously noted with unidentate **1** with platinum or palladium, the aldehydic proton is situated above the coordination plane in a position axial to the metal. For the platinum complex **108**, a downfield shift (1.62 ppm) relative to **89a** and an

unusually large J_{Pt-H} (13.7 Hz) was realized [76]. The distorted square-planar geometry of the platinum center and the directed aldehydic hydrogen toward the platinum atom (H–Pt bond length, ca. 2.3 Å) in **108** was confirmed by X-ray data [74,75].



108



109

Immediately after the previous paper appeared, Risen et al. [77] reported the formation of a brown hydrido complex **109** via the oxidative addition of **89a** to the Pt(0) complex [PtP(cyclohexyl)$_3$(C_2H_4)$_2$] (**110**); treatment of **109** with CCl_4 produced **106d**, the tricyclohexylphosphine analog of **106b**. The structure of **109** was supported by the ν(C=O) at 1621 cm^{-1} in the IR and the Pt–*H* signal at δ −2.86 with $J_{(P-H)} = 23$ Hz and $J_{(Pt-H)} = 1170$ Hz in the ^{1}H NMR spectrum.

E. CONCLUSIONS

The use of model 8-(substituted)quinolines for the study of reactions at metal centers has received limited attention. The *N*-coordination allows the formation of chelated intermediates, after the initial reaction or insertion has taken place, thus providing sufficient stability (usually) for isolation and identification of the intermediates.

The work of Deeming with 8-alkyl derivatives and of Suggs with the 8-carbonyl derivatives, for the most part, has provided a solid understanding of the basic mechanisms of the different, but complimentary processes of insertions into C(sp^3)–X and C(sp^2)–X (X = C or H) bonds. It is anticipated that as new reactions involving related metal catalysts are developed, appropriate 8-(substituted)quinolines will be synthesized and used to unravel future important mechanisms.

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