Pentacarbonyl[ethoxy(2-buten-1-yl)carbene]tungsten (13). A solution of 1.23 g (1.89 mmol) of **12** in 100 mL methylene chloride was treated at 0 °C with 2.0 mL of a 1 M methylene chloride solution of triethyloxonium tetrafluoroborate over 10 min. The mixture was stirred for additional 0.5 h at 0 °C. The solvent was removed in vacuo, and the residue stirred for 1 h in 100 mL of *n*-hexane. A precipitate was filtered off, and the solution concentrated to one-quarter volume. $W(CO)_6$ was filtered off, and the solution was cooled to −30 °C to crystallize residual $W(CO)_6$. The solution was decanted, and the solvent evaporated. The residue was dried in vacuo (0.5 h) to give 400 mg (49%) **13** as a red brown oil. ^{1}H NMR spectroscopy revealed a 40:60 mixture of cis and trans isomer. Anal. Calcd for $C_{12}H_{12}O_6W$ (436.1): C 33.05, H 2.77. Found: C 33.29, H, 2.66. ^{1}H NMR (C_6D_6, mixture of isomers) δ 5.56–5.10 (m, 2 H, H2 and H3 of cis and trans isomer), 4.36 (q, 2 H, OCH_2CH_3 of cis and trans isomer), 3.67 (br d, H1(c)), 3.55 (br d, H1(t); together with H1(c), 2 H), 1.47 (dq, H4(t)), 1.43 (ddt, H4(c); together with H4(t), 3 H), 0.94 (t OCH_2CH_3(t)), 0.92 (t, OCH_2CH_3(c); together with trans isomer, 3 H), coupling constants (Hz), *trans*-**13**, ^3J = 6.7 (H1, H2) 6.1 (H3, H4) 7.1 (OCH_2CH_3), ^4J = 1.2 (H2, H4), ^5J = 0.9 (H1, H4), *cis*-**13**, ^3J = 7.0 (H1, H2) 6.7 (H3, H4) 7.1 (OCH_2CH_3), ^4J = 1.7 (H2, H4), ^5J = 0.9 (H1, H4). ^{13}C NMR (C_6D_6, mixture of isomers) δ 330.4, 330.3 (C-carbene(c,t)), 203.3 (C–CO_{trans}(c,t)), 197.6 (C–CO_{cis}(c,t)), 130.4 (C3(t), 153), 127.7 (C3(c), 149), 123.7 (C2(t), 158), 122.6 (C2(c), 159), 80.6 (OCH_2CH_3(c,t), 149), 68.1 (C1(t), 128), 62.9 (C1(c), 129), 17.9 (C4(t), 120) 14.1 (OCH_2CH_3(c,t), 127), 13.2 (C4(c), 127), the resonances of the ethoxy group and the metal carbonyl carbons were not resolved. IR (NaCl, mixture of isomers) 2070, 1978 (sh), 1936 (v strong) cm^{-1}. MS (EI), 436 ($M^{+\cdot}$, 28), 323 (100), 295 (81), 268 (49).

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Registry No. **2**, 93403-16-8; **3**, 124535-63-3; **4a**, 126823-70-9; **4b**, 126823-69-6; **5**, 126823-71-0; **7a**, 85924-65-8; **7b**, 85924-69-2; **8**, 126823-72-1; **9**, 1617-32-9; **10**, 126823-74-3; **11**, 126823-75-4; **12** (isomer 1), 126823-77-6; **12** (isomer 2), 126923-06-6; **13** (isomer 1), 126823-78-7; **13** (isomer 2), 126923-07-7; $(Cp_2ZrO)_3$, 70693-90-2.

Mechanistic Aspects of the Cyclometalation of Quinoline-8-carboxaldehyde with Platinum(II)

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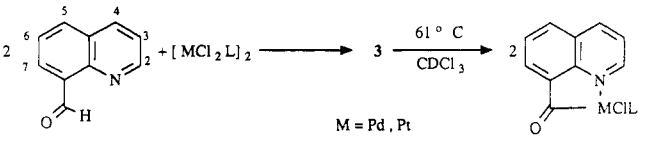
Rates of reaction at 61 °C in $CDCl_3$ for the cyclometalation of quinoline-8-carboxaldehyde (**1**) with *trans*-$PtCl_2$(**1**)L (L = PEt_3, PBu^n_3, PPh_3, $PTol_3$, $AsEt_3$, $AsPr^i_3$, $AsTol_3$) are reported. Starting from *trans*-$PtCl_2$(**1**)(PEt_3), there is a kinetic isotope effect k_H/k_D = 1.4. Modification of the Pt(II) complex to *trans*-$PtBr_2$(**1**)L enhances the rate by a factor of ca. 70. The use of *sym-trans*-$[Pt(\mu\text{-Cl})(SnCl_3)(PTol_3)]_2$ and 2 equiv of **1** affords facile cyclometalation at room temperature within the mixing time. The direct generation of cationic complexes via *cis*-$PtCl_2L_2$ plus $Ag(CF_3SO_3)$ followed by addition of **1** is also shown to lead to facile cyclometalation. All of these reactions are discussed in terms of the importance of cationic metal compounds. Synthetically, the most efficient cyclometalation of **1** can be accomplished by using $[Pt(\mu\text{-Cl})(\eta^3\text{-}CH_2C(CH_3)CH_2)]_2$. ^{1}H and ^{31}P NMR data are given for selected examples.

Introduction

The cyclometalation reaction is now a well-known synthetic method for creating metal–carbon bonds.[1] Despite this, there are not many studies concerned with its mechanistic detail[2] and most of these are related to palladium chemistry.[3] We have been involved in the cyclometalation of various aldehyde ligands[4a] and have observed a facile metalation of quinoline-8-carboxaldehyde (**1**) using both Pd(II) and Pt(II).[4b] The chemistry of eq 1 contains at least two well-defined steps, as do many cyclometalations,[1] the first of which involves the room-temperature reaction of the dimer with 2 equiv of **1** to afford *trans*-MCl_2(**1**)L (**3**, which has an interesting M–H–C interaction[5,6]) and subsequent cyclometalation at 61 °C in chloroform.



1 **2** **4**

M = Pt, L = PEt_3 (**4a**), $PTol_3$ (**4b**), PPh_3 (**4c**), $AsEt_3$ (**4d**), $AsTol_3$ (**4e**), $AsPr^i_3$ (**4f**)

(1)

Despite the relative ease of this reaction and the known[7] oxidative addition of **1** to Rh(I), it is not certain which

(1) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327. Bruce, M. K. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73. Constable, E. C. *Polyhedron* **1984**, *3*, 1037.

(2) Thompson, J. M.; Heck, R. F. *J. Org. Chem.* **1975**, *40*, 2667. Bruce, M. I.; Goodall, B. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 687. Stolzenberg, A. M.; Muetterties, E. L. *Organometallics* **1985**, *4*, 1739. Lewis, L. N. *Inorg. Chem.* **1985**, *24*, 4433. Lewis, L. N. *J. Am. Chem. Soc.* **1986**, *198*, 743.

(3) (a) Ryabov, A.; Sokodynskaya, I. K.; Yotsimirsky, A. K. *J. Chem. Soc., Dalton Trans.* **1985**, 2629. (b) *J. Chem. Soc., Perkin Trans. 2* **1983**, 1511.

(4) (a) Motschi, H.; Pregosin, P. S.; Rüegger, H. *J. Organomet. Chem.* **1980**, *193*, 397. (b) Anklin, C. G.; Pregosin, P. S. *J. Organomet. Chem.* **1983**, *243*, 101.

(5) Anklin, C. G.; Pregosin, P. S. *Magn. Reson. Chem.* **1985**, *23*, 671.

(6) Albinati, A.; Anklin, C. G.; Pregosin, P. S. *Inorg. Chim. Acta* **1984**, *90*, L37.

(7) Suggs, J. W.; Wovkulich, M. J.; Cox, S. D. *Organometallics* **1985**, *4*, 1101. Suggs, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 640.

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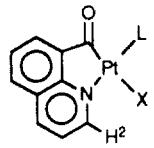
Table I. Selected NMR Data[a] for the Acyl Complexes



L	X	$\delta(H^2)$	$\delta(^{31}P)$
PEt_3	Cl	10.32 (27.1)	16.3 (4446)
PBu^n_3	Cl	10.32 (26.5)	7.5 (4455)
PPh_3	Cl	10.41 (31.2)	21.4 (4887)
$PTol_3$	Cl	10.43 (30.3)	20.0 (4844)
$AsEt_3$	Cl	10.28 (35.3)	
$AsPr^i_3$	Cl	10.41 (35.3)	
PPh_3	Br	10.72 (30.0)	
$PTol_3$	Br	10.62 (28.9)	
$PTol_3$	I	11.3 (32.1)	21.7 (4817)
DIPHOS			44.6 (1548)
CF_3SO_3			34.9 (4123) [^2J(P,P) = 5.8 Hz]
DIPHOS			44.5 (1539)
BPh_4			34.7 (4099) [^2J(P,P) = 6.9 Hz]
1,5-COD			
CF_3SO_3		9.55 (42.5)	

[a] For $CDCl_3$ solutions, unless otherwise specified; ^{195}Pt coupling constants in parentheses (in Hz).

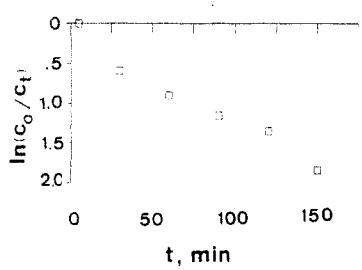


Figure 1. Plot of ln (c_0/c_t) vs time t (minutes) for the cyclometalation of *trans*-$PtCl_2(1)(PTol_3)$ at 61 °C in $CHCl_3$ (c_t = concentration of complex at time t).

factors promote this Pt(II) chemistry. We report here on the relative kinetics of this cyclometalation, including the kinetic isotope effect k_H/k_D, and extend our results to similar cyclometalation reactions of 1 derived from (a) the cationic complexes $PtCl(1)L_2^+$ (L = PEt_3, $PTol_3$ (Tol = C_6H_4-*p*-CH_3), $^1/_2$ 1,5-COD (COD = cyclooctadiene), $^1/_2$ $Ph_2PCH_2CH_2PPh_2$ (DIPHOS)), (b) trichlorostannate complexes, and (c) $[Pt(\mu\text{-}Cl)(\eta^3\text{-}CH_2(CH_3)CH_2)]_2$ and Zeise's dimer.

Results and Discussion

***trans*-$PtCl_2(1)L$ System.** Several of the complexes 4 have been prepared previously,[5] and the remaining few have been synthesized in an analogous fashion. For 4 with M = Pd and L = PPh_3, we have determined the structure by X-ray diffraction, in combination with ^1H and ^{31}P NMR data for solution studies.[8] The geometry in solution is the same as that determined in the solid; for the platinum complexes this is mirrored in the relatively large ^1J(Pt,P) spin–spin coupling of >3 kHz. For a different geometry, i.e., PR_3 trans to the acyl ligand, the value would be considerably smaller.[9]

The disappearance of 3 and the development of 4 is conveniently followed by ^1H NMR spectroscopy (see the supplementary material). The aldehyde proton of the coordinated ligand appears at relatively low field, δ = 13.09, as do the signals from H^2 in both 3 and 4. As the reaction requires several hours to run its course at 61 °C, the quenching to 0 °C followed by measurements at room temperature slows the product development such that the ^1H integrals serve to follow the disappearance and appearance of these resonances. In Table I we present some NMR data for our complexes, whereas Table II shows kinetic data.

Table II. Rates for the Cyclometalation Reactions

substrate	comments	k, 10^{-5} s^{-1}	k_{rel}
trans-$PtCl_2(1)L$			
L = PEt_3		5.2	1.0
L = PEt_3	+1 equiv of $Pr^i_2N(CHEt_2)$	5.8	1.1
L = PEt_3	+1 equiv of 1	4.2	0.8
L = PEt_3	in refluxing acetone	4.4	0.8
L = PEt_3	1 deuterated at aldehyde	3.5	0.7
L = PBu^n_3[a]		4.9	0.9
L = $PTol_3$		17.1	3.4
L = $PTol_3$	refluxing acetone	19.0	3.6
L = PPh_3		27.0	5.2
L = PPh_3	$CDCl_3$/MeOH-d_4 (2:1), 60 °C	76.6	14.7
L = PPh_3[a]	$CDCl_3$/acetone-d_6 (2:1), 0.25 equiv of $SnCl_2$, 60 °C	75.3	14.5
L = $AsEt_3$		9.6	1.8
L = $AsPr^i_3$		2.0	0.4
L = $AsTol_3$		21.7	4.2
trans-$PtBr_2(1)L$			
L = PEt_3[a]		348	68
L = $PTol_3$		400	70
L = PPh_3[a]		400	70
trans-$PdCl_2(1)(PEt_3)$		3.9	0.7
$[Pt(\mu\text{-}Cl)Cl(PEt_3)]_2$	0 °C	3	0.6
$[Pt(\mu\text{-}Cl)Cl(PPh_3)]_2$	0 °C	18.2	3.6
$[Pt(\mu\text{-}Cl)(SnCl_3)(PTol_3)]_2$	0 °C	12.9	2.5
cis-$PtCl_2(PEt_3)_2$	1 equiv of Ag^+,[b] 1 equiv of 1, room temp, acetone/CH_2Cl_2 (2:1)	58.8	11.3
cis-$PtCl_2(PEt_3)_2$	1 equiv of Ag^+,[b] 2 equiv of 1, room temp, acetone/CH_2Cl_2 (1.5:1)	45.8	8.8
cis-$PtCl_2(PTol_3)_2$	1 equiv of Ag^+,[b] 1 equiv of 1, room temp, acetone/CH_2Cl_2 (2:1)	4.8	0.9
cis-$PtCl_2$(DIPHOS)	1 equiv of Ag^+,[b] 2 equiv of 1, 60 °C, acetone/CH_2Cl_2 (1.5:1)	10.4	2

[a] Average result from two different experimenters, ±15%. [b] Data obtained via ^{31}P NMR spectroscopy; $Ag(CF_3SO_3)$.

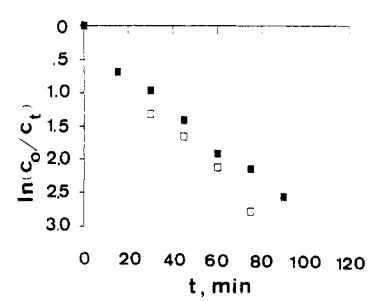


Figure 2. Plot of ln (c_0/c) vs time t (minutes) for $[PtCl(solvent)(PEt_3)_2]^+$ plus 1 to afford $PtCl(1)(PEt_3)_2^+$, which then cyclometalates (room temperature): (open squares) [Pt]/[1] = 1; (closed squares) [Pt]/[1] = 0.5.

(8) Albinati, A.; Anklin, C. G.; Ganazolli, F.; Rüegg, H.; Pregosin, P. S. Submitted for publication in *Inorg. Chem.*
(9) Albinati, A.; von Gunten, U.; Pregosin, P. S.; Rüegg, H. *J. Organomet. Chem.* **1985**, *295*, 239.

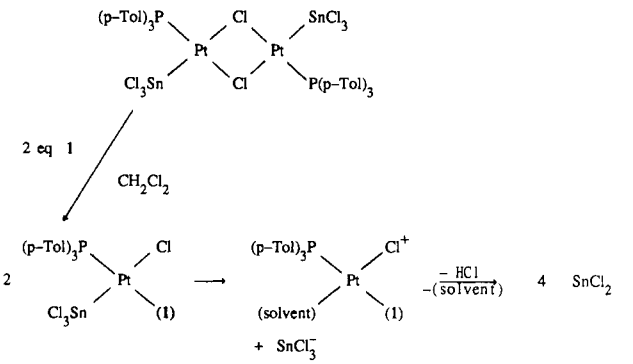
The cyclometalation reaction is first order in **3**, which is obtained quantitatively from **1** and **2**, as demonstrated by plots of ln (c_0/c) vs time (c_0 = initial concentration of **3**; see Figures 1 and 2). The reaction rate is not significantly dependent on the presence of a base in that addition of either the tertiary aliphatic amine $Pr^i_2N(CHEt_2)$ or an additional 1 equiv of **1** does not markedly change the kinetics. Inspection of the rate dependence on arsine and phosphine ligands reveals a change of ca. a factor of 13, with $AsPr^i_3$ the slowest and PPh_3 the fastest. Despite this difference, it is not immediately obvious that steric effects alone are inhibiting, in that the smaller $AsEt_3$, is somewhat slower than $AsTol_3$. Moreover, $PTol_3$, which is larger than PEt_3 but a poorer donor,[10] accelerates the reaction. In acetone solvent the PEt_3 and $PTol_3$ analogues react at about the same speed as in chloroform. Interestingly, for L = PEt_3 the Pt(II) and Pd(II) complexes cyclometalate at about the same rate. Of interest is the kinetic isotope effect k_H/k_D = 1.4 for the cyclometalation of *trans*-$PtCl_2(1)(PEt_3)$ (deuterated **1** was prepared by reacting 8-bromoquinoline with DMF-d_7; see the Experimental Section), and we shall return to this value shortly. The most significant effect on the kinetics arises from substitution of Br for Cl, which affords a 65–70-fold increase in rate such that the reaction is almost too fast for monitoring by room-temperature ^1H NMR spectroscopy. The obvious extension to the iodide complex proved surprising in that—at first glance—the kinetics for L = $PTol_3$ are slower. Closer inspection shows that the rate decrease is associated with a change in the rate-determining step. Whereas bridge splitting in eq 1 to give **3** is facile with both the Cl and Br dimeric starting materials, for the I complex this reaction is now slow. Using ^1H NMR spectroscopy to monitor the reaction, we observe no *trans*-$PtI_2(1)(PTol_3)$ in solution but only **1**, *sym-trans*-$[Pt(\mu\text{-}I)I(PTol_3)]_2$, *and the product acyl compound.* This suggests that the conversion of the presumed *trans*-$PtI_2(1)(PTol_3)$ to the iodide analogue of **4b** is indeed facile and perhaps faster yet than for the bromo analogue. It is possible that the softer Br and I ligands enhance the electron density at the metal; however, there is mass spectral and vibrational spectroscopic evidence for Pt^{II}–X strengths such that Pt–I < Pt–Br < Pt–Cl.[11] Moreover, since the better donor PEt_3 reacts slower than either $AsEt_3$ or $PTol_3$, we were not convinced of an oxidative-addition mechanism and considered the possibility that halogen dissociation might be important. To this end we measured the rate for L = PPh_3 in 2:1 $CDCl_3/CD_3OD$. It is reasonable that the methanol might (a) stabilize a cationic complex if it were formed and (b) hydrogen bond to the departing halide, thereby stabilizing this anion via solvation; indeed, the result was a rate enhancement of a factor of 2.8. These results do not prove a halogen dissociation mechanism, but they are suggestive. An attempt to generate a cation directly from *trans*-$PtCl_2(1)(PPh_3)$ and $Ag(CF_3SO_3)$ afforded partial decomposition, thereby complicating the analysis; consequently, we chose a somewhat indirect route to a related species and show this chemistry in eq 2.

$$[PtCl_2(PPh_3)]_2 + 1 + n\,SnCl_2 \xrightarrow[CDCl_3/\text{acetone-}d_6\ 2:1]{60\,^\circ C} \text{Products} \quad (2)$$

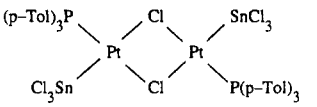
$n = 0.2;\ 0.5;\ 1.0$

(10) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953, 2956. Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(11) Haake, P.; Mastin, S. H. *J. Am. Chem. Soc.* **1971**, *93*, 6823 and references therein.

Scheme I

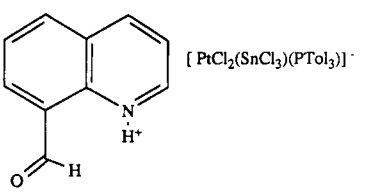


Addition of $SnCl_2$ to complexes that contain a Pt–Cl linkage usually leads to the Pt–$SnCl_3$ moiety.[8,12-15] $SnCl_3$ can dissociate[10] to afford Pt^+ and $SnCl_3^-$, and in some chemistry this is considered to be of fundamental importance.[16,17] We chose the $CDCl_3$/acetone solvent mixture to ensure a homogeneous solution, as $SnCl_2$ is only sparingly soluble in $CDCl_3$ and, as noted above, we know that the cyclometalation in acetone proceeds at a rate comparable to that in $CDCl_3$. Reaction 2 is also 2.8 times faster in the presence of $SnCl_2$ than the analogous chemistry in its absence. This rate enhancement prompted us to consider beginning from the preformed trichlorostannate complex **5**. We have previously prepared[18] a series of such



5

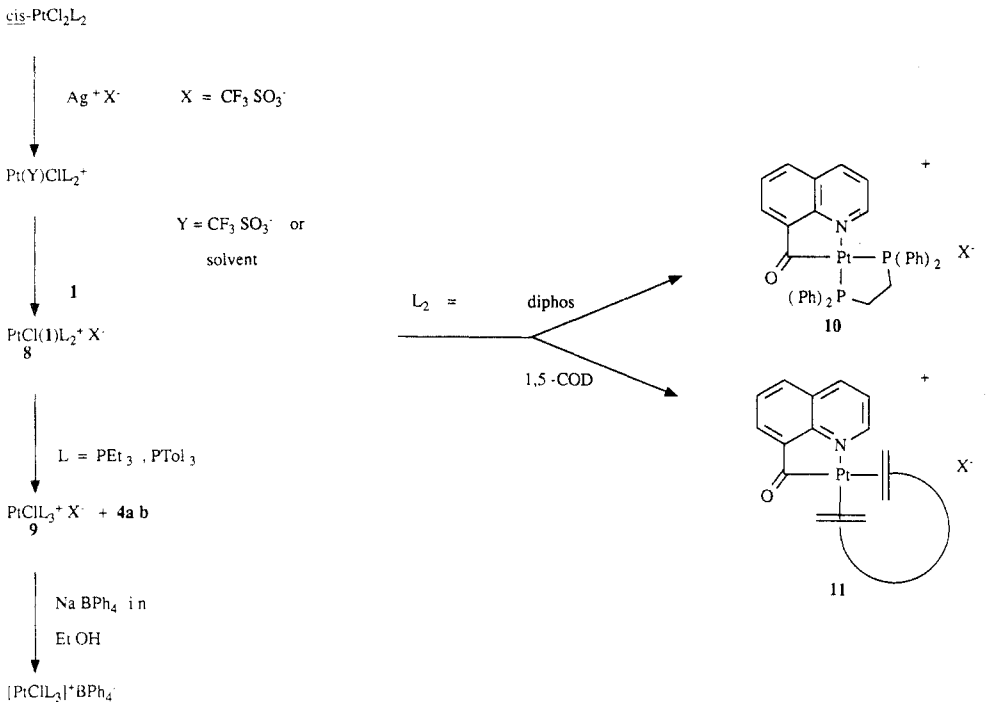
complexes and have determined the structure of $[Pt(\mu\text{-}Cl)(SnCl_3)(PEt_3)]_2$.[19] Compound **5** is the potential precursor of $PtCl(SnCl_3)(1)(PTol_3)$ (**6**), and we do know[20] that complexes of type **5** react with 2 equiv of *p*-chloroaniline and *p*-toluidine to give aniline analogues of **6**. Derivative **5** reacts with **1** *at 0 °C* at the same rate as that of $[Pt(\mu\text{-}Cl)Cl(PTol_3)]_2$ at 60 °C. The products are the known cyclometalated species **4b** and the anionic complex **7**[12b] in a ca. 1:1 ratio.



7

(12) Herbert, I. R.; Pregosin, P. S.; Rüegger, H. *Inorg. Chim. Acta* **1986**, *112*, 29. Rüegger, H. *Inorg. Chem.* **1984**, *23*, 3223. Ostoja Starzewski, K. H. A.; Pregosin, P. S.; Rüegger, H. *Helv. Chim. Acta* **1982**, *65*, 785.
(13) Nelson, J. H.; Cooper, V.; Rudolph, R. W. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 263. Holt, M. S.; MacDougall, J. J.; Mathey, F.; Nelson, J. H. *Inorg. Chem.* **1984**, *23*, 449.
(14) Koch, B. R.; Fazakerley, G. V.; Dijkstra, E. *Inorg. Chim. Acta* **1980**, *45*, L51.
(15) Kingston, J. V.; Scollary, G. R. *J. Chem. Soc. A* **1971**, 3765.
(16) Anderson, G. K.; Clark, H. C.; Davies, J. A. *Organometallics* **1982**, *1*, 64. Clark, H. C.; Kurosawa, H. *Inorg. Chem.* **1972**, *11*, 1275. Clark, H. C.; Jablonski, C. R.; Halpern, J.; Mantovani, A.; Weil, T. A. *Inorg. Chem.* **1974**, *13*, 1541.
(17) Ammann, C.; Pregosin, P. S.; Rüegger, H.; Grassi, M.; Musco, A. *Magn. Reson. Chem.* **1988**, *27*, 355.
(18) Pregosin, P. S.; Rüegger, H. *Inorg. Chim. Acta* **1984**, *86*, 55.
(19) Albinati, A.; Näegeli, R.; Starzewski, K. H. A.; Pregosin, P. S.; Rüegger, H. *Inorg. Chim. Acta* **1983**, *76*, L231.
(20) Albinati, A.; Moriyama, H.; Rüegger, H.; Pregosin, P. S.; Togni, A. *Inorg. Chem.* **1985**, *24*, 4430.

Scheme II



The structure of **7** was determined by using ^{1}H, ^{31}P, ^{119}Sn, and ^{195}Pt NMR methods. We envision the reaction to proceed as shown in Scheme I, which we intend as illustrative but not definitive. Independent reaction of $[Pt(\mu\text{-}Cl)Cl(PPh_3)]_2$ with 2 equiv each of **1** and $Ph_4P^+Cl^-$ affords $PtCl_3(PPh_3)^-$ as its Ph_4P^+ salt, so that a 1:1 ratio of **4b** and **7** is understandable in that once Cl^- is generated via cyclometalation, it consumes half the platinum in the form of the anion of **7**. $PtCl_3(PPh_3)^-$ reacts with $SnCl_2$ to afford $PtCl_2(SnCl_3)(PPh_3)^-$ (and even some $PtCl(SnCl_3)_2(PPh_3)^-$).

Before we comment on all of this chemistry, it is worth considering the cyclometalation of **1** via the cations $PtCl(1)L_2^+$.

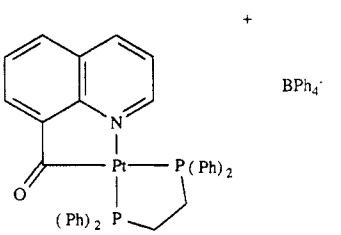
***cis*-$PtCl_2L_2$ System.** A number of studies have shown that mono- and dications stemming from $PtCl_2L_2$ molecules show enhanced reactivity.[27] In view of the previous discussion we have carried out the reaction sequence shown in eq 3 and Scheme II.

$$cis\text{-}PtCl_2L_2 + Ag(CF_3SO_3) \xrightarrow{1} \underset{8}{PtCl(1)L_2^+} \longrightarrow \text{Products} \quad (3)$$

L = PEt_3, P(p-Tol)$_3$ or 1/2 Diphos, 1,5-COD.

All of the reactions lead to cyclometalation of the aldehyde at the carbonyl. The PEt_3 and P(*p*-Tol)$_3$ derivatives lead to the known complexes **4a,b**, whose identity we could confirm via ^{31}P NMR spectroscopy. Since this cationic chemistry is new, we present some of the spectroscopic details and begin by noting for **4a,b** that the observed large (>4400 Hz) $^{1}J(Pt,P)$ value is typical for a tertiary phosphine trans to the quinoline nitrogen and cis to the acyl function. Both the cis and trans effects are important, as $^{1}J(Pt,P)$ for PR_3 trans to the quinoline nitrogen in **7** is much smaller.[6] In addition to **4a,b**, 50% of the starting material is converted to the known[22] cations $PtClL_3^+$ (L = PEt_3, P(Tol)$_3$). The relative reaction rate for L = PEt_3 is ca. 11 times faster at room temperature than that starting from *trans*-$PtCl_2(1)(PEt_3)$ at 60 °C. Clearly, the cyclometalation at the aldehyde carbon is enhanced by a cationic metal center.

The appearance of the tris(phosphine) cation suggested that PR_3 loss from **8** may have importance. Consequently, we repeated the chemistry of eq 3 using $PtCl_2$(DIPHOS), in the hope of suppressing phosphine dissociation. Cyclometalation to afford complex **10** occurs but is once again



relatively slow; K_{rel} = 2 at 60 °C. Cation **10**, as its BPh_4 salt, shows two distinct ^{31}P resonances, δ = 44.5 ($^{1}J(Pt,P)$ = 1538 Hz) and δ = 34.7 ($^{1}J(Pt,P)$ = 4099 Hz, $^{2}J(P,P)$ = 7 Hz), which are part of an AX (AMX with ^{195}Pt) spin system. These two very different $^{1}J(Pt,P)$ values are consistent with an acyl ligand trans to P^1 but cis to P^2. The acyl carbonyl function shows a stretch at 1640 cm^{-1}. Although the reduced rate with $PtCl_2$(DIPHOS) is not advantageous, there is no loss of platinum due to $PtClL_3^+$ formation, and this makes the chelate approach synthetically slightly more attractive.

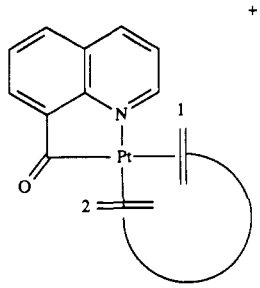
To make the platinum yet more electrophilic, the chelating 1,5-COD was introduced as $PtCl_2$(COD), plus Ag(CF_3SO_3), with gratifying results. The cyclometalation reaction proceeds smoothly at −5 °C to yield **11** in 65% yield. The reaction at room temperature leads to decomposition.[23] Compound **11** was identified by ^{1}H NMR and IR spectroscopy and microanalysis. We note the two

(21) Davies, J. A.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 79. Hartley, F. R.; Murray, S. G.; Wilkinson, A. *Inorg. Chem.* **1989**, *28*, 549.

(22) Favez, R.; Roulet, R.; Pinkerton, A. A.; Schwarzenbach, D. *Inorg. Chem.* **1980**, *19*, 1356.

(23) We have tried K[$PtCl_3(C_2H_4)$] plus **1** and find only decomposition to Pt(0) at room temperature. We have also not been able to control this reaction with $PtCl_2$(1,5-COD); however, we do not exclude the possibility that a similar reaction occurs.

(24) De Jong, F.; Bour, J. J.; Schlebos, P. P. J. *Inorg. Chim. Acta* **1988**, *154*, 89.



11

different Pt,H coupling constants, arising when our acyl chelate is present, in this case $^2J(Pt,H)$ = 25.4 and 74.9 Hz, for the olefin protons H^1 and H^2, respectively, due to the different trans influence of the acyl and nitrogen functions.

The enhanced rates of these cyclometalations, and especially that for $PtCl_2$(1,5-COD), speak in favor of electrophilic attack of the metal on the carbonyl function. However, along with the increased electrophilicity, due to positive charge, comes an increase in the lability of the coordination sphere, which leads to additional coordinative unsaturation (remember the formation of the $PtClL_3^+$ cations). We considered it likely that these ideas might be combined via the use of allyl or monodentate olefin complexes and chose as test substrates $[Pt(\mu\text{-}Cl)\{\eta^3\text{-}CH_2C(CH_3)CH_2\}]_2$ *and Zeise's dimer*, $[Pt(\mu\text{-}Cl)Cl(C_2H_4)]_2$. Both of these compounds contain π-acceptor ligands of moderate σ-donor capacity, and the Cl bridges assure the nitrogen of 1 easy access to the metal. Both react cleanly at room temperature to give $[Pt(\mu\text{-}Cl)(NC_9H_6CO)]_2$ (**12**) in high yield, with the π-allyl complex being somewhat faster in 89% yield. Complex **12** is sparingly soluble but

$$[Pt(\mu\text{-}Cl)\{\eta^3\text{-}CH_2C(CH_3)CH_2\}]_2 + 2(1) \longrightarrow 12 \qquad (4)$$

shows an IR stretch at 1645 cm^{-1} typical for an acyl carbonyl bound to Pt(II)[4] (the carbonyl stretch for **1** is much higher). Further, **12** reacts at room temperature with PR_3 to give the known compounds **4**. Conversion of the phosphine complexes **3** to **4** requires several hours at 61 °C in $CHCl_3$, thereby confiriming that this conversion from **12** to **4** is not a cyclometalation of the aldehyde but, rather, a simple bridge-splitting reaction. From a synthetic point of view the π-allyl complex provides the cleanest and simplest approach to the cyclometalation of **1**. Low-temperature ^1H NMR spectroscopy for reaction 3 shows that two isomers, due to the relative orientations of the methallyl CH_3 and CHO groups, of $PtCl(1)\{\eta^3\text{-}CH_2C(CH_3)CH_2\}$ (**13**) are formed cleanly in solution at ca. −60 °C in CD_2Cl_2; however, above −30 °C the cyclometalation reaction begins and the kinetics could not be readily followed due to substantial line broadening. Consequently, we cannot say with certainty if η^3–η^1 isomerization is important for this reaction; however, molecules related to **13** are known and studies of their dynamics[25] suggest that η^3–η^1 processes have a higher activation energy.

Conclusions

Summarizing, we have shown that (a) ligand **1** can be readily cyclometalated at the aldehyde carbon, (b) the rate of this reaction can be increased by about 2 orders of magnitude by a judicious choice of accompanying ligand and charge on the complex, and (c) there is circumstantial evidence that the platinum electrophilically attacks the carbonyl and this brings us to the kinetic isotope effect described above. In keeping with the literature,[3a,26] we consider 1.4 to be a primary isotope effect and interpret this difference in rate to imply some C–H bond breaking in the rate-determining step.[27] The transition state is not likely to be linear, so that a relatively modest k_H/k_D value is reasonable. We cannot say if precoordination of the carbonyl function is important. In view of the presumed electrophilic nature of the attack, and our knowledge of the ground-state structure of *trans*-$PtCl_2(1)(PEt_3)_2$, in which the C–H vector faces the platinum,[7] we consider that complexes containing small π-acceptor ligands, combined with easy access of the nitrogen to the metal, correctly tune this type of cyclometalation.

Table III. ^{31}P NMR Data[a] for $[PtClL_3]Y$ Complexes

L	Y⁻	δ(P)	$^1J(Pt,P)$, Hz	δ(P′)	$^1J(Pt,P')$, Hz	$^2J(P,P')$, Hz
PEt_3[b]	CF_3SO_3	9.9	3456	18.4	2262	19.8
PEt_3	BPh_4	9.0	3441	17.4	2268	19.6
PR^n_3[c]	CF_3SO_3	−1.4	3473	8.5	2254	19.2
$PTol_3$	CF_3SO_3	10.1	3645	21.4	2472	18.5
$PTol_3$	BPh_4	10.7	3639	22.0	2470	19.1

[a] In $CDCl_3$ unless otherwise specified; P trans to Cl, P trans to P′. [b] In acetone-d_6, 0 °C. [c] In CD_2Cl_2.

Experimental Section

All preparations were carried out under nitrogen. Quinoline-8-carboxaldehyde was prepared as described previously, as were the necessary dimeric complexes $[Pt(\mu\text{-}Cl)ClL]_2$. Typically kinetic runs with these complexes were carried out as follows:

A solution of *sym-trans*-$[Pt(\mu\text{-}Cl)ClL]_2$ (0.07 mmol) in 6 mL of $CDCl_3$ was placed in a round-bottom flask and then treated with 1 (0.022 g, 0.14 mmol) and the ^1H NMR reference material 1,3,5-trimethoxybenzene (0.005 g, 0.03 mmol). The flask was then placed in an oil bath (75 °C) and the solution refluxed. At regular intervals 0.4 mL of solution was removed and cooled to 0 °C (or below) and then a ^1H NMR spectrum measured at room temperature (total measuring time ca. 10 min). The initial concentration of the formed intermediates $PtCl_2(1)L$ was ca. 2.3×10^{-2} M in all cases. The analysis of the relative integrals affords the data given in Table I. We estimate that these rates are correct to ±15%. For this system the reaction kinetics follow the simple equation $\ln (c_0/c_t) = kt$; c_0 = initial concentration, c_t = concentration at time t (see Figure 1).

Reactions Involving Cations. Reactions of the cations $PtCl(solvent)L_2^+$ were studied preparatively before the kinetic investigation. *cis*-$PtCl_2(PTol_3)_2$ (0.17 g, 0.20 mmol) in 2 mL of 1:1 acetone/CH_2Cl_2 was treated with a solution of $Ag(CF_3SO_3)$ (0.051 g, 0.20 mmol) in 0.5 mL of acetone. The resulting suspension was stirred at room temperature for 0.5 h and then filtered through Celite into a solution of **1** (0.031 g, 0.20 mmol) in 0.5 mL of CH_2Cl_2. Stirring for 2 h was followed by removal of the solvents and addition of 10 mL of EtOH. The resulting solution was then treated with a solution of $NaBPh_4$ (0.34 g, 1.0 mmol) in 10 mL of EtOH and the precipitate that formed collected via filtration. This solid is $[PtCl(PTol_3)_3][BPh_4]$ (0.13 g, 45%) and corresponds to ca. 50% of the platinum not consumed via cyclometalation. The cyclometalated acyl complex was recognized via its ^{31}P NMR characteristics. ^{31}P NMR data for the $PtClL_3^+$ cation are shown in Table III.

$[Pt(NC_9H_6CO)(DIPHOS)][BPh_4]$. $PtCl_2$(DIPHOS) (0.11 g, 0.20 mmol) in 2 mL of 1:1 acetone/CH_2Cl_2 was treated with $Ag(CF_3SO_3)$ (0.51 g, 0.20 mmol) in 0.5 mL of acetone. The resulting suspension was filtered through Celite into a solution of **1** (0.031 g, 0.20 mmol) in 0.5 mL of CH_2Cl_2 and the resulting

(25) Vrieze, K. In *Dynamic NMR Spectroscopy*; Academic Press: London, 1975; p 441. Faller, J. W. *Adv. Organomet. Chem.* **1977**, *16*, 211.

(26) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732. Smith, G.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1984**, 1203. Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814.

(27) We cannot exclude a mechanism whereby halogen dissociation is slow and a following faster (but still slow) attack at the C–H bond occurs. Since this second step might be associated with a very large k_H/k_D ratio, the net result might be a very moderate isotope effect.

solution refluxed for 80 min. Removal of the solvents in vacuo afforded an oil, which was dissolved in 10 mL of EtOH and then treated with $NaBPh_4$ (0.068 g, 0.20 mmol) also in 10 mL of EtOH. Addition of *n*-pentane induced precipitation of the product (0.070 g, 34%).

[Pt(NC$_9$H$_6$CO)(1,5-COD)](CF$_3$SO$_3$). $PtCl_2$(1,5-COD) (0.10 g, 0.30 mmol) was dissolved in 2 mL of 1:1 EtOH/CH_2Cl_2 and then treated with a solution of $Ag(CF_3SO_3)$ (0.15 g, 0.60 mmol) in 1 mL of EtOH. Stirring of the suspension at room temperature for 60 min and then cooling to −20 °C was followed by filtration through Celite into a precooled (−20 °C) solution of 1 (0.084 g, 0.60 mmol) in 2 mL of EtOH. The precipitate that formed was immediately filtered (under nitrogen) and dried to afford the product (0.12 g, 65%). Anal. Calcd for $C_{19}H_{18}NF_3O_4PtS$: C, 37.50; H, 2.98; N, 2.30. Found: C, 37.05; H, 2.93; N, 2.61.

The kinetics for the cationic complexes were measured by using ^{31}P NMR spectroscopy ($c_0 = 3.3 \times 10^{-2}$ M with O←PPh_3 as the reference in a $CDCl_3$ capillary). Typically, *cis*-$PtCl_2L_2$ (0.1 mmol) was dissolved in 1 mL of 1:1 acetone/CD_2Cl_2. Addition of $Ag(CF_3SO_3)$ (0.025 g, 0.10 mmol) in 0.5 mL of acetone gave a suspension, which was stirred for 30 min. Cooling to −60 °C was followed by filtration over Celite into a precooled (−60 °C) solution of 1 (16 mg, 0.10 mmol) in 1 mL of CD_2Cl_2. A ^{31}P spectrum was measured at −60 °C; the sample was shaken at room temperature for 15 min, recooled to −60 °C, at which temperature there is little or no reaction, and then monitored via ^{31}P NMR spectroscopy. A plot of ln ($c_0 - c_t$) vs t for L = PEt_3 is shown in Figure 2.

Quinoline-8-carboxaldehyde-*d*. 8-Bromoquinoline (2.66 g, 12.8 mmol) was dissolved in 12 mL of THF and the solution cooled to −78 °C. Treatment with 1.5 equiv of butyllithium (9.2 mL of a 2 M solution) in hexane and stirring for 10 min at −78 °C was followed by fast addition of 1.2 mL of DMF-d_7. Warming to room temperature and destroying excess butyllithium with acid was followed by extraction with ether. This removes nonbasic organic impurities. The aqueous solution was then made basic and once again extracted with ether. Drying of this second ether layer was followed by concentration in vacuo to afford the crude product, which was recrystallized from water (890 mg, 45%; 99.2% D labeled). ^2H NMR: δ = 11.5 (CDO). ^{13}C NMR: δ = 192.5 (CDO, $^1J(^{13}C,^2H)$ = 28.7 Hz).

Preparation of [Pt(μ-Cl)(NC$_9$H$_6$CO)]$_2$. The π-allyl dimer [Pt(μ-Cl){$CH_2C(CH_3)CH_2$}]$_2$ (25 mg, 0.04 mmol) was dissolved in 1 mL of CH_2Cl_2. Solid quinoline-8-carboxaldehyde (13.8 mg, 0.08 mmol) was added to this solution, with the result that a red-brown precipitate immediately formed (27.5 mg, 89%). Anal. Calcd for $C_{20}H_{12}H_2O_2Cl_2Pt_2$: C, 31.06; H, 1.56; N, 3.62; Cl, 9.17. Found: C, 30.35; H, 1.58; N, 3.54; Cl, 9.16.

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Supplementary Material Available: Partial NMR spectra of 1 and *trans*-$PtCl_2$(1)(PEt_3) and NMR spectra showing the disappearance of **3a** and the development of **4a** (2 pages). Ordering information is given on any current masthead page.

Reaction of Nickel(0) with α-Keto Phosphonates. Syntheses, Characterization, and X-ray Crystal Structure of $(PPh_3)_2Ni(\eta^2\text{-}(CO)RC(O)P(O)(OMe)_2)$

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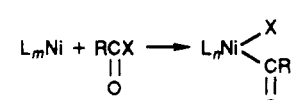
Reaction of Ni(1,5-cyclooctadiene)$_2$ with α-keto phosphonates in the presence of PPh_3 affords $(PPh_3)_2Ni(\eta^2\text{-}(CO)RC(O)P(O)(OMe)_2)$ (R = phenyl, **1**; *p*-tolyl, **2**; *p*-chlorophenyl, **3**; methyl, **4**; ethyl, **5**), characterized by IR, ^1H NMR, and ^{31}P NMR spectra. The single-crystal X-ray diffraction of **5** [monoclinic, $P2_1/n$, a = 9.640 (3), b = 18.910 (8), c = 20.821 (8) Å, β = 90.03 (3)°, V = 3796 (2) Å^3, Z = 4, R_1 = 0.049] has revealed that ethyl keto phosphonates coordinate to the Ni(PPh_3)$_2$ moiety in an η^2-CO mode, making the Ni geometry square planar. These complexes undergo exchange reaction of α-keto phosphonate ligand in solution. Judging from the π-coordination ability of α-keto phosphonates toward Ni(0), a P(O)(OMe)$_2$ group has been estimated to be electronegative by as much as a CF_3 group.

Introduction

Zerovalent nickel complexes are very reactive toward many organic compounds. Especially, the reaction with organic compounds containing acyl groups (RC(O)Z) is interesting because the reaction pattern depends on the substituent (Z) on the acyl carbon. Acyl halides (Z = halogen) undergo oxidative addition to give (acyl)(halide)nickel complexes (eq 1).[4] Carboxylic esters (Z = OR′)



(1)

undergo either oxidative addition at the RCO–OR′ bond to a Ni(0) complex to give an (acyl)(alkoxy or aryloxy)nickel complex (eq 2) or oxidative addition at the RCOO–R′ bond to give a (carboxylato)(alkyl or aryl)nickel complex

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(4) (a) Otsuka, S.; Nakamura, A.; Yoshida, T.; Naruto, M.; Ataka, K. *J. Am. Chem. Soc.* **1973**, *95*, 3180. (b) Heimback, P.; Jolly, P. W.; Wilke, G. *Adv. Organomet. Chem.* **1970**, *8*, 29.

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