J. King Saud Univ., Vol. 9, *Science* (1), pp. 65-75 (A.H. 1417/1997)

Synthesis and Characterization of Some Rhodium (III) Cyclometallated Schiff's Base Complexes Derived from 2-Benzylidene Amino-Substituted Pyridines

Hassan B. Amin

Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

(Received 1/1/1996; accepted for publication 16/6/1996)

Abstract. A series of rhodium complexes of the type [RhHCl{(2-hydroxy benzylidene)(X-pyridine)}$(PPh_3)_2$] have been synthesized and spectroscopically characterized.

The Schiff's base derived from X-2-aminopyridines (X=H,3-Me, 4-Me, 5-Cl or 3,5-Br) substituents and 2-hydroxybenzaldehyde reacted with either [RhCl$(PPh_3)_3$] or [Rh(μ-Cl)(cycloocta-1,5-diene)]$_2$ in the presence of four equivalents of triphenylphosphine to give the corresponding rhodium(III) cyclometallated complexes, in which the imine C-H bond has added oxidatively to the metal. The complexes have been isolated, and characterized by IR, U.V., ^{1}H-, ^{13}C- and ^{31}P- NMR spectroscopy. The IR and ^{1}H NMR spectral data show that the hydride ligand is *trans* to a N-donor ligand. The ^{13}C chemical shifts for the carbon atom bonded to Rh all fall in the range 235-238 ppm, whereas, those for the corresponding carbon in the uncomplexed imine are found at 160-170 ppm.

Introduction

The synthesis and reactions of cyclometallated complexes formed by the cleavage of C-C and C-H bonds of organic molecules in homogeneous mdeia is a rapidly growing research area. Many metals have been found to insert into C-H and/or C-C bonds [1-4]. Among the platinum group metal complexes used to study the activation of these bonds, platinum [5,6], palladium [5-7], rhodium and iridium [8,9] complexes have been found to be effective. A significant amount of work has been done on the heterocyclic aromatic species 8-substituted quinolines [5,11-14] and 2-(benzylidenamino) pyridines [8,9, 15-17]. Complexation of the metal with nitrogen in arylamines results in a favorable geometry for insertion of the metal into a neighboring C-H or C-C bond [8, 9, 11, 18].

The synthesis and characterization of some new rhodium (III) complexes of [2-benzylideneamino] pyridines, in which the imine C-H has undergone oxidative addition to the metal, are reported below.

$$2-(HO)C_6H_4CHO + X_{-2}-H_2NC_5H_3N \xrightarrow{-H_2O} 2-HOC_6H_4CH=N(2)C_5H_3N(X)$$

Experimental

Substituted pyridines, 2-hydroxybenzaldehyde, $RhCl_3$ x H_2O, PPh_3 and cyclo-1, 5-octadiene were obtained from Winlab, Aldrich Chemicals, and Strem Chemicals respectively, and were used as received.

Preparation of the Schiff's bases

A solution of equivalent amounts of the substituted 2-aminopyridines and 2-hydroxybenzaldehyde in MeOH (70 cm^3) was boiled under reflux with stirring for 2 h at 80°C. The solvent was then taken off in a rotary evaporator to leave a yellow liquid. This was treated with n-hexane to precipitate the crude product, which was then recrystallized from absolute ethanol. The melting points, yields, elemental analyses are listed in Table 1. $[Rh(\mu\text{-}Cl)COD)]_2$ and $[RhCl(PPh_3)_3]$ were prepared according to the reported procedures [19, 20; p. 380].

Preparation of the cyclometallated Schiff's base complexes (Scheme 1)

The rhodium(III) complexes were prepared by reaction of the Schiff's base with either $[RhCl(PPh_3)_3]$ or with $[Rh(\mu\text{-}Cl)COD)]_2$. Two typical examples are described below.

(1) A solution containing $[RhCl(PPh_3)_3]$ (300 mg, 0.325 mmol) and an equivalent amount of Schiff's base in ca. 20 cm^3 of dry THF was boiled under reflux for 1h under nitrogen then allowed to cool. Addition of n-hexane precipitated the product as yellow solid, which was filtered off (and could be recrystallized from CH_2Cl_2/hexane).

(2) A solution of $[Rh(\mu\text{-}Cl)(COD)]_2$ (200 mg, 0.28 mmol), the Schiff's base (0.56 mmol) and PPh_3 (293 mg, 1.12 mmol) in ca. 20 cm^3 of dry THF was boiled under reflux for 1 h. Addition of n-hexane precipitated the product, which was filtered off (and could be recrystallized from CH_2Cl_2/hexane). The colors, melting points, yields, elemental analyses and recrystallization solvents are listed in Table 2.

Spectroscopy

U.V. -Vis. spectra were recorded on a Pu-8800 Pye Unicam Philips spectrometer using spectroscopic grade solvents (MeOH, EtOH and $CHCl_3$). I.r. spectra, of KBr pellets, were recorded on a Perkin-Elmer 783 spectrophotometer. N.m.r. spectra were recorded at 26°C on Jeol JNM Ex-400 spectrometer with deuterium locking. The $^{13}C\{^1H\}$ spectra were

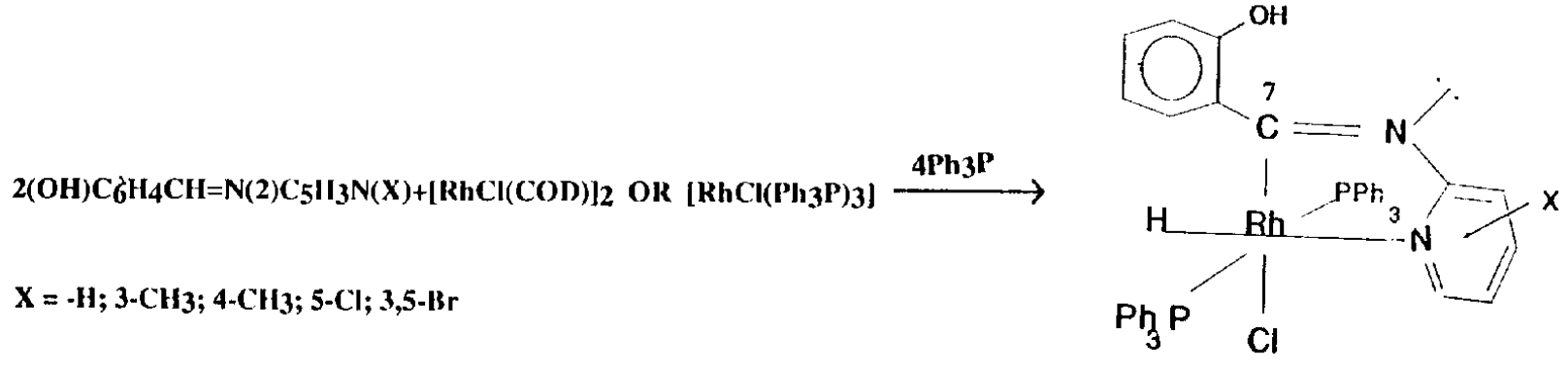
Table 1. Physical and analytical data for the Schiff's bases

x	M.P.°C	Yield	Molecular formula	Calculated (%) C	H	N	Found (%) C	H	N
H	67.0	96	$C_{12}H_{10}N_2O$	72.71	5.09	14.17	72.65	4.96	14.07
3-Me	83.6	76	$C_{13}H_{12}N_2O$	73.56	5.7	13.2	73.47	5.57	13.24
4-Me	100.0	70	$C_{13}H_{12}N_2O$	73.56	5.7	13.2	73.63	5.82	13.34
6-Me	66.5	71	$C_{13}H_{12}N_2O$	73.56	5.7	13.2	73.45	5.66	13.15
4,6-Me	85.0	95	$C_{14}H_{14}N_2O$	74.31	6.24	12.38	74.28	6.11	12.39
5-Cl	118.0	94	$C_{12}H_9N_2OCl$	61.93	3.9	12.04	61.84	3.78	12.12
6-Cl	173.0	95	$C_{12}H_9N_2OCl$	61.93	3.9	12.04	61.75	3.75	12.43
3,5-Br	170.0	73	$C_{12}H_9N_2OBr_2$	40.48	2.27	7.87	40.62	2.14	7.57

Table 2. Physical and analytical data for the cyleometallated complexes

X	Complex	Color	M.P°C	Solvent of recryst.	Yield %	Calculated (%) C	H	N	Found (%) C	H	N
H	$C_{48}H_{40}N_2OP_2Rh$	Yellow	225	CH_2Cl_2 hexane	15	69.82	4.88	3.39	69.74	4.77	3.34
3-CH3	$C_{49}H_{42}N_2OP_2Rh$	Yellow	209-210	"	12	70.08	5.04	3.34	70.12	4.94	3.38
4-CH3	$C_{49}H_{42}N_2OP_2Rh$	Yellow	266	"	17	70.08	5.04	3.34	70.14	5.14	3.27
5-Cl	$C_{48}H_{39}N_2OClP_2Rh$	Yellow	349	"	17	67.02	4.57	3.26	67.12	4.48	3.34
3,5-Br	$C_{48}H_{38}N_2OBr_2P_2Rh$	Yellow	279	"	16	58.62	3.89	2.85	58.63	3.89	2.76

Complex Synthesis



(Scheme 1)

recorded at 100.53 MHz, the ^{1}H-n.m.r. spectra at 399.78 MHz and the ^{31}P{1H} spectra at 161.86 MHz. Chemical shift data for ^{13}P spectra are given relative to 85% H_3PO_4 (external), more positive values representing deshielding. The solvent for the cyclometallated compounds was $CDCl_3$.

Results and Discussion

Insertion of metals into C-H bond have been observed with both quinoline and Schiff base substrates [1]. Complexes bringing this about include $RhCl(PPh_3)_3$, $[RhX_2Cl]_2$ ($X=C_2H_4$ or CO), $[MCl(\mu\text{-}Cl)L]_2$ (M=Pd(II) or Pt(II) and L=phosphines), and $[M(\mu\text{-}Cl)(cyclooctene)_2]_2$ [(M=Ir(I) or Rh)(I)] [5, 11, 14, 15-17]. However, insertion into a C-C bond has been reported only for the quinoline series, and is apparently a more demanding reaction [11, 14], both sterically and electronically. Results in this series indicate that while the previous complexes bring about insertion in a C-H bond, they are not all effective for that into a C-C bond. By far, the most effective complex for insertion into the C-C bond is the ethylene complex $[Rh(C_2H_4)_2Cl)]_2$, which has been shown to insert into the C-C bond in a variety of Q-C(O)R ketones [10] (Q= 8-Quinolyl; R= $-CH_3$, $-C_2H_5$ and C_6H_5). Formation of the product from insertion into the C-C bond is rendered irreversible by displacement of the ethylene ligand with pyridine. Suggs *et al.* [13, 15-17] have rationalized these results on the basis of the reactivity of the ligand. Thus, if the product of insertion into the C-C bond is treated with a strong σ-bonding ligand such as a phosphine or carbon monoxide, the reaction is reversed and a Rh(I) complex is regenerated. There is also evidence to indicate that the greater rigidity of the 8-substituted quinoline molecules makes them more favorable for insertion into the C-C bond than the more flexible 2-(benzylidenamino) pyridines. However, even in the quinoline series, if other reactions are possible they tend to be favored over C-C bond insertion.

The ^{1}H NMR spectrum of each of the new rhodium complexes in $CDCl_3$ shows a hydride resonance between δ-11.37 and δ -11.69 ppm (Table 3). The imine C-H signals for the starting imines apear at δ 9.37 - 9.44. and after complexation these signals are absent, providing evidence for insertion of Rh complex into the C-H bond of the imine.

Table 3. ^{1}H and ^{31}P N.M.R. chemical shifts for the cyclometallated complexes

Complex No.	X	^{1}H Hydride (ppm)	^{31}P {^{1}H} (ppm)	$^2J(^{31}P\text{-}^1H)$ (Hz)	$^1J(^{103}Rh\text{-}^1H)$ (Hz)	$^1J(^{103}Rh\text{-}^{31}P)$ (Hz)
(1)	H	– 11.37	28.82	11.68	13.50	102.54
(2)	3-CH_3	– 11.38	28.40	11.69	12.83	102.54
(3)	4-CH_3	– 11.46	28.70	11.82	12.83	103.43
(4)	5-Cl	– 11.46	29.61	11.40	14.50	102.54
(5)	3,5-Br_2	– 11.69	29.60	11.50	15.50	102.54

Strong confirmation eivdence comes from appearance of the resonance of the hydride signal in each complex at high field [18, 21], ca.δ - 12.0 ppm. The hydride signals in the complexes are split by coupling to two equivalent ^{31}P nuclei and the ^{103}Rh nucleus. As both of these spin-spin couplings are frequently ca. 12.0 Hz, the hydride multiplet often appears as a pseudo quartet, but higher resolution studies usually reveal the expected doublet of triplets (Fig. 1). The PPh_3 rhodium complexes show a ^{31}P signal at ca. δ 28.4 - 29.6 with $^{1}J(^{103}Rh\text{-}^{31}P)$ 102.54 - 103.43 Hz (Fig. 2) in keeping with previous reports [18; p. 156]. The majority of the rhodium imine hydride complexes are only moderately soluble in most organic solvents.

The signal of -^{13}C=N of the imino group is observed at δ 235.56-237.60 (Table 4). The $^{13}C\{^{1}H\}$ NMR spectrum, in particular the signal from the metal-bonded carbon atom, is consistent with the presence of the cyclometallated ring [18, 23]; the signal from the metal-bonded carbon, C(7) appears as a doublet of triplets (Fig. 3) owing to coupling

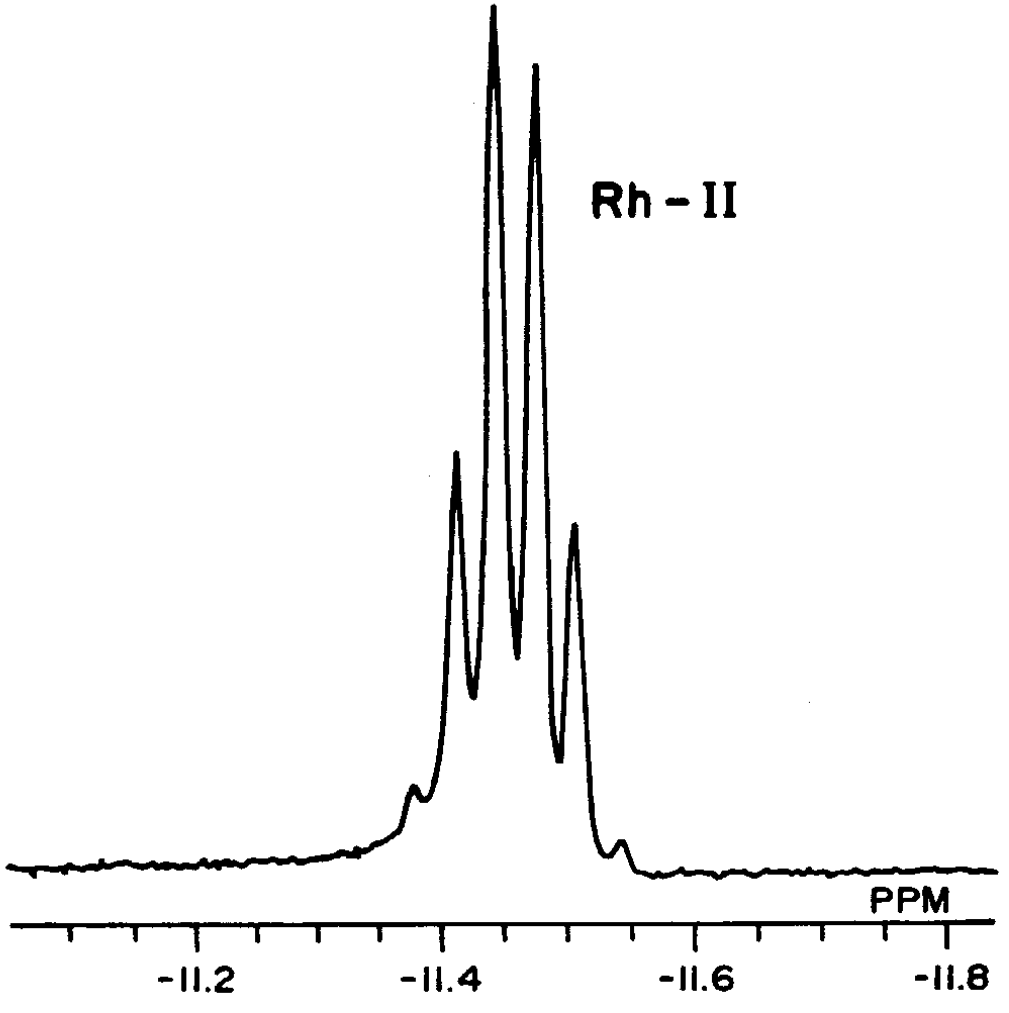


Fig. 1. 400 MHz ^{1}H NMR of 0.1M in $CDCl_3$ at 21°C for complex (1).

Table 4. ^{13}C {^{1}H} data for C(7) in the cyclometallated complexes[a]

Complex No.	X	δ C(7)	$^{1}J(^{103}Rh^{13}C)$	$^{2}J(^{31}P - ^{13}C)$
(1)	H	236.89	35	7
(2)	3-CH3	235.56	35	7
(3)	4-CH3	236.24	35	7
(4)	5-Cl	237.60	35	7

a δ in ppm, J in Hz

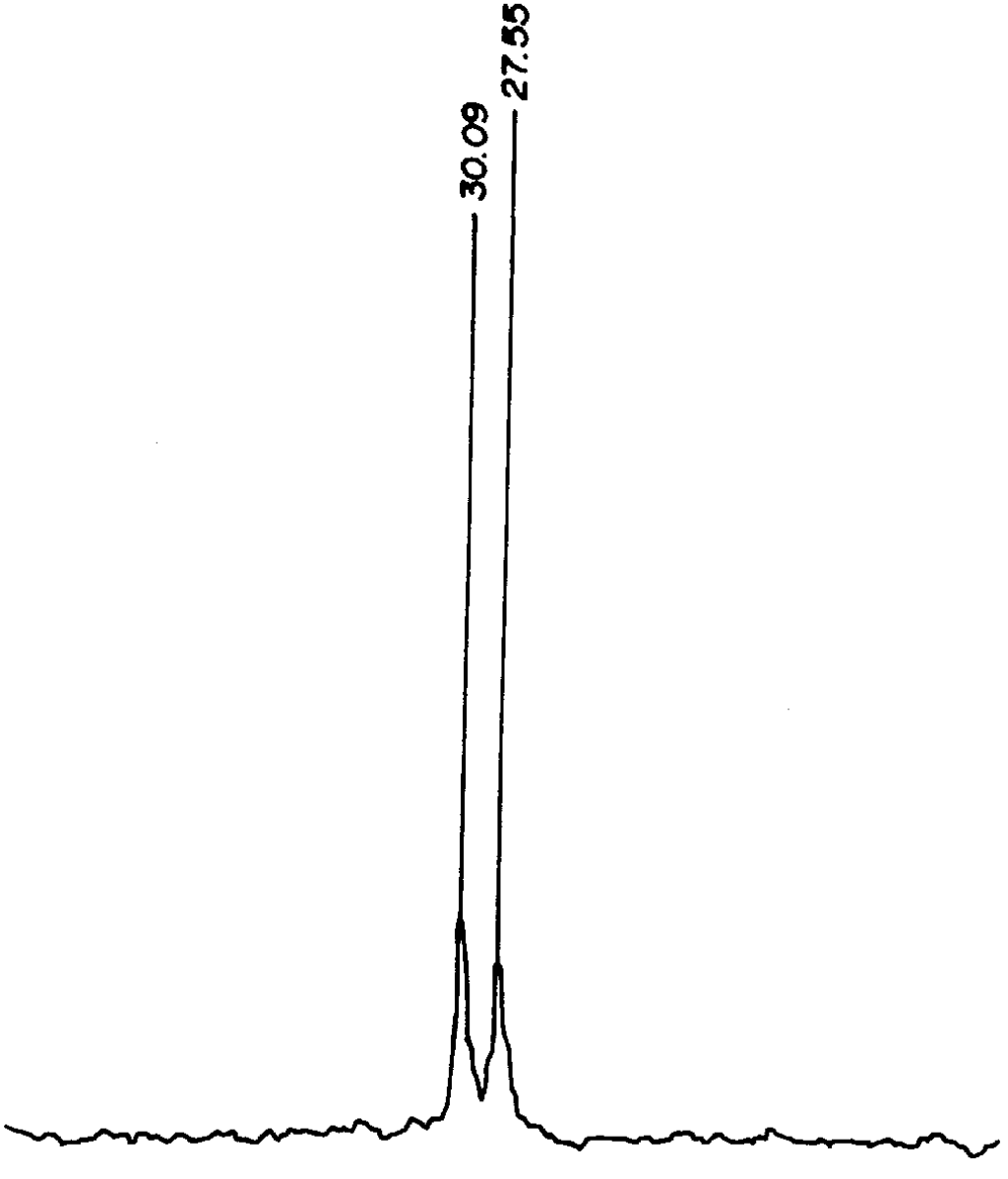


Fig. 2. 400 MHz $^{31}P\{^{1}H\}$ NMR spectra of complex (1) in $CDCl_3$ relative to 85% H_3PO_4 (external).

to two equivalent ^{31}P nuclei and the ^{103}Rh nuclei, whereas the corresponding signal from the uncomplexed imine is found at δ 158.11 - 163.99 ppm [23]. This low-field position for C(7) has been observed in other cases in what a chelating atom is incorporated in a five membered-ring [24], and is not unusual for a cyclometallated sp^2 carbon [25; p. 238, 26, 27]. The remaining ^1H and ^{13}C NMR data are as expected.

The positions of the ligand signals in both the IR (ν Rh-H 2040 cm^{-1}) and ^1H NMR (δ -11.37 to -11.69) spectra, are as expected for a Rh-H bond trans to an N-donor ligand [28, 29]. Furthermore, the $^2J(^{31}P\text{-}^1H)$ value is consistent with a hydride located *cis* to two magnetically equivalent PPh_3 groups [30], which in turn are mutually trans, as inferred from the ^{31}P [^1H] NMR spectrum.

It is noteworthy that attempts to prepare related complexes from Schiff's bases, derived from benzaldehyde and 3-aminopyridines, or 2-aminopyridines (those with X=6-CH_3, 4,6$(CH_3)_2$, 6-Cl), were unsuccessful. No sign of reaction was observed, and this may be due to steric or inductive effects of the substituent on the pyridine ring.

Acknowledgement. The author would like to thank the Research Center, College of Science, King Saud University, for the financial support to this project (Chem./1409/02).

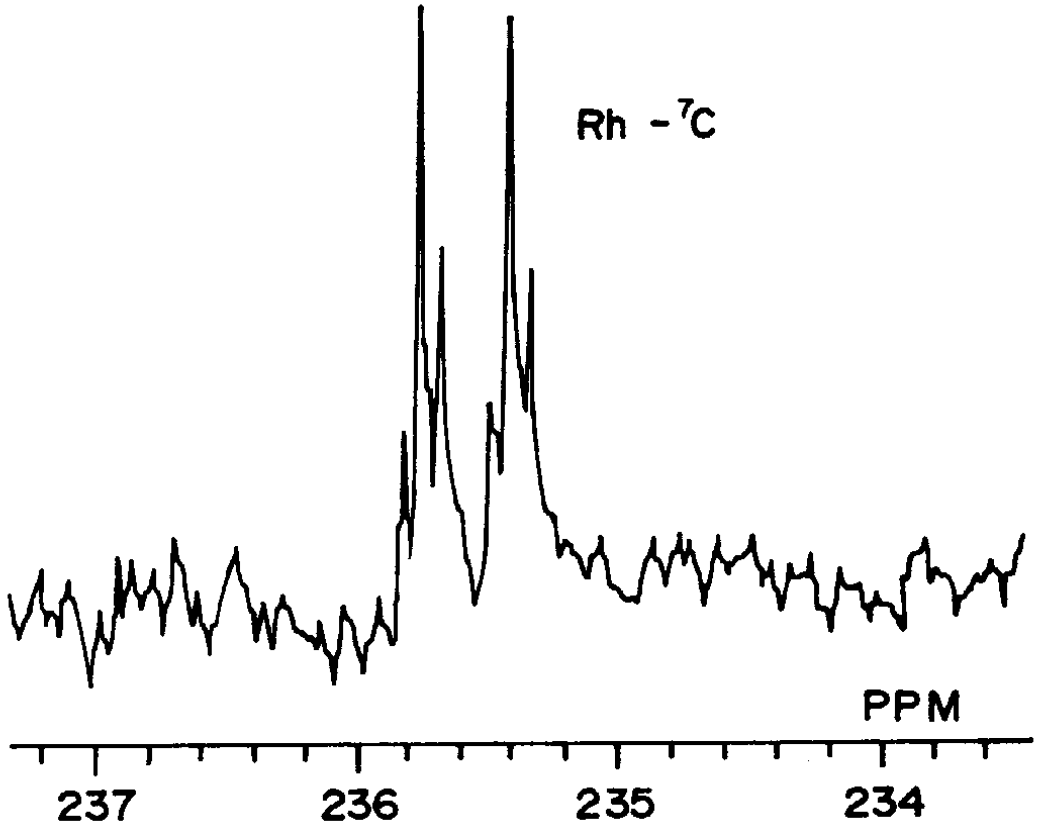


Fig. 3. 400-MHz ^{13}C NMR of 0.1M in $CDCl_3$ at 21°C for complex (1).

References

[1] Dehand, J. and Pfeffer, M. "Cyclometallated Compounds." *Coord. Chem. Rev.*, 18 (1976), 327-352.

[2] Omae, I. "Organometallic Intramolecular-Coordination Compounds Containing a Nitrogen Donor Ligand." *Chem. Rev.*, 79, No. 4 (1979), 287-321.

[3] Omae, I. "Organometallic Intramolecular-coordination Compounds: Recent Aspects in the Study of Sulfur Donor Ligands." *Coord. Chem. Rev.*, 28 (1979), 97-115.

[4] Bosque, R., Lopez, C., Sales, J., Tramuns, D. and Solans. X. "Activation of σ (C-H) Bonds in Ferrocenyl -and bis(ferrocenyl) Imines Promoted by Palladium." *J. Chem. Soc., Dalton Tans.* 14 (1995), 2445-2452.

[5] Albinati, A., Anklin, C.G., Ganazzoli, F., Ruegg, H. and Pregosin, P.S. "Preparative and ^{1}H NMR Spectroscopic Studies on Palladium(II) and Platinum(II) Quinoline-8-carbaldehyde(1) Complexes. X-ray Structures of the Cyclometalated Acyl Complex $PdCl(C(O)C_9H_6N)(Ph_3)PPh_3$ and trans-$PtCl_2$ (1)(PEt_3)." *Inorg. Chem.*, 26 (1987), 503-508.

[6] Albinati, A., Arz, C. and Pregosin, P.S. "nJ(Pt,H) and Pt-H-C Interactions in Schiff Base Complexes of 2-(Benzylideneamino)-3-methylpyridine. Molecular Structures of Dichloro(2-(2,4,6-trimethylbenzylidene)amino)-3-methylpyridine)triethylarsine) platinum(II) and Dichloro (2-amino-3-methylpyridine)triethyl phosphine)palladium(II)." *Inorg. Chem.*, 26 (1987), 508-513.

[7] Janecki, T., Jeffreys, J.A.D., Pauson, P.L., Pietrzykrowski, A. and McCullough, K.J. "Bis-Ortho-Metalated Palladium Complexes. New Examples and Reactivity. The X-ray Crystal Structure of *cis*-(2-C_6H_5N=$NC_6H_4)_2Pd$ and cis-(2-C_6H_5N=NC_6H_4))(2-$Me_2NCH_2C_6H_4$)Pd." *Organometallics*, 6 (1987), 1553-1560.

[8] Sprouse, S., King, K.A., Spellane, P.J., Watts, P. and Richard, J."Photophysical Effects of Metal-carbon Sigma Bonds in Orthometalated Complexes of Iridium(III) and Rhodium(III)." *J. Am. Chem. Soc.*, 106, No. 22 (1984), 6647-6653.

[9] Perera, S.D., Shaw, B.L. and Thornton-Pett, M. "General Strategy for Inducing C-H bond Fission (Cycloiridation) in Some Aryl, Heterocyclic, Alkenyl or Alkyl Groups in azines Derived from Aldehydes or Methyl ketones." *J. Chem. Soc., Dalton Trans.*, 10 (1995), 1689-1696.

[10] Crabtree, R.H. "The Organometallic Chemistry of Alkanes." *Chem. Rev.*, 84, No. 4 (1985), 245-269.

[11] Suggs, J.W., Wovkulich, M.J. and Cox, S.D. "Synthesis, Structure and Ligand-promoted Reductive Elimination in an Acylrhodium Ethyl Complex." *Organometallics*, 4, No. 6 (1985), 1101-1107.

[12] Garber, A.R., Garron, P.E., Hartwell, G.E., Smas, M.J., Wilkinson, J.R. and Todd, L.J. "Application of Carbon-13 NMR to the Determination of Metal-carbon. Sigma Bond Formation in Cyclometalation Reactions with Nitrogen Donor Ligands." *J. of Organomet. Chem.*, 86, No. 2 (1975), 219-227.

[13] Suggs, J.W. and Chul-Ho, J. "Metal-catalysed Alkyl Ketone Conversions in Chelating Ketones via Carbon-Carbon Bond Cleavage." J. *Chem. Soc., Chem. Commun.*, (1985), 92-93.

[14] Dowerah, D., Radonovich, L.J., Woolsey, N.F. and Heeg, M.J. "Reaction of 2-((alpha-R-Benzylidene)amino)pyridines LBR equals CH//3, 4-(CH//30)C//6H//4] with RhCl(L)//3 or Rh//2Cl//2(CO)//4. Formation and Structure of a Rhodium(II) Dimer." *Organometallics*, 9, No. 3 (1990), 614-620.

[15] Suggs, J.W. "Activation of Aldehyde Carbon-hydrogen Bonds to Oxidative Addition via Formation of 3-Methyl-2-aminopyridyl Aldimines and Related Compounds: Rhodium Based Catalytic Hydroacylation." *J. Amer. Chem. Soc.*, 101, No. 2 (1979), 489.

[16] Suggs, J.W. and Chul-Ho, J. "Synthesis of a Chiral Rhodium Alkyl via Metal Insertion into an Unstrained C-C Bond and Use of the Rate of Racemization at Carbon to Obtain a Rhodium-Carbon Bond Dissociation Energy." *J. Amer. Chem. Soc.*, 108 (1986), 4679-4681.

[17] Suggs, J.W. and Chul-Ho, J. "Directed Cleavage of Carbon-carbon Bonds by Transition Metals: the alpha-Bonds of ketones." *J. Amer. Chem. Soc.*, 106, No. 10 (1984), 3054-3056.

[18] Albinati, A., Arz, C. and Pregosin, P.S. "Synthesis, Structure and NMR Spectroscopy of some Rhodium(III) Cyclometalated Schiff's Base Complexes Derived from 2-Benzylidene-3-

methylpyridines. Crystal Structure of (RhHI(2(3-nitrobenzylidene)-3-methyl- pyridine) (RhHI(2-(3-nitrobenzylidene)-3-methyl-pyridine) (PPh3)2)." *J. Organomet. Chem.*, 35, No. 3 (1987), 379-394.

[19] Giordano, G. and Crabtree, R.H. "Di-mu.-chloro-bis(*.eta.*4-1,5-cyclooctadiene)dirhodium(I)." *Inorg. Synth.*, 19 (1979), 218-220.

[20] Colquhonn, H.M., Holton, J., Thomspon, D.J. and Wigg, M.V. *New Pathways for Organic Synthesis. Practical Application of Transition Metals.* New York: Plenum Press, 1984.

[21] El-Baih, F.E.M., Abu-Loha, F.M., Gomma, Z. and Al-Najjar, I.M. "Synthesis and Characterization of Some Rhodium(III) Cyclometallated Complexes of 2-substituted benzylideneamino Thiazoles." *Trans. Met. Chem.*, 19, No. 3 (1994), 325-328.

[22] Pregosin, P.S. and Kunz, R.W. "Phosphorus-31 and Carbon-13 NMR of Transition Metal Phosphine Complexes." *N.M.R. Basic Principle and Progress.* Berlin: Springer Verlag, 1979.

[23] Al-Najjar, I.M., Al-Showiman, S.S. and Al-Hazmi, H.M. "Multinuclear NMR Studies on New Platinum Imine Complexes." *Inorg. Chim. Acta*, 89, No. 1 (1984), 57-63.

[24] Garrow, P.E. "ΔR Ring Contributions to ^{31}P NMR Parameters of Transition-Metal-Phosphorus Chelate Complexes." *Chem. Rev.*, 81 (1981), 229-266.

[25] Mann, B.E. and Taylor, B.F. ^{31}P NMR Parameters of Transition-Metal-Phosphorus Chelate Complexes." Chem. Rev., 81 (1981), 229-266.

[26] Foot, R.J. and Heaton, B.T. "Metallation of 2-Vinylpyridine by Rhodium(III)." *J. Chem. Soc.*, Chem. Commun. (1973), 838-839.

[27] Nomura, Y. and Takeuchi, Y. "Double Inversion at Two Nitrogen Atoms in Bicyclic Hydrazines. A ^{15}N Nuclear Magnetic Resonance Study." *J. Chem. Soc., Chem. Commun.* (1979), 295-296.

[28] Crabtree, R.H. and Lavin, M. "Carbon-hydrogen and Hydrogen-Hydrogen Bond Activation: Dissociative versus nondissociative Binding to Iridium." *J. Chem. Soc., Chem.* Commun., 12 (1985), 794-795.

[29] Lanfredi, A.M.M., Tripicchio, A., Ugozzoli, F., Ghedini, M. and Neve, F. "Iridium(III) cis-Dihydrido Complexes with 3,6-Bis(2'-pyridyl)pyridazine. Crystal Structure of the Pyridazinyl Complex $[\{IrH_2(PPh_3)_2\}_2\{\mu\text{-}C_4HN_2(C_5H_4N)_2\text{-}3,6\}]PF_6$." *J. Chem., Soc., Dalton Trans.* (1988), 651-673.

[30] Kaesz, H.D. and Saillant, R.B. "Hydride Complexes of the Transition Metals." *Chem. Rev.*, 72, No. 3 (1972), 231-281.

تحضير ووصف بعض معقّدات قواعد شيف المحلقنة المعدنية للروديوم (III) المشتقة من ٢ - بنزيليدين أمينو - بديل بيريدينات

حسان بكر أمين

قسم الكيمياء، كلية العلوم، جامعة الملك سعود، ص. ب ٢٤٥٥ ،
الرياض ١١٤٥١ ، المملكة العربية السعودية

(استلم في ١٠ شعبان ١٤١٦هـ؛ قبل للنشر في ٣٠ محرم ١٤١٧هـ)

ملخص البحث. تم تحضير وتوصيف سلسلة من معقّدات الروديوم من النوع [RhHCl {(2-hydroxybenzylidene) (X - Pyridine)} (PPh_{32})] وذلك بتفاعل قاعدة شيف المشتقة من ٢ - أمينو بيريدين المحتوي على بدائل و ٢ - هيدروكسي بنزالدهيد مع أي من $[RhCl(PPh_3)_3]$ أو [Rh(μ-Cl) (Cycloocta - 1,5 - diene)]$_2$ في وجود أربع مكافئات من ثلاثى فينيل الفوسفين لإعطاء معقّد محلقن معدني للروديوم (III) ، وفيه وجد أن رابطة C-H أضيفت بشكل مؤكسد للمعدن . عزلت المعقّدات وتم التعرف عليها باستخدام أطياف الأشعة تحت الحمراء وفوق البنفسجية وطيف الرنين النووي المغناطيسي للهيدروجين ^{1}H- ، الكربون ^{13}C- والفسفور ^{31}P- . وجد أنه الموضع الجديد للهيدريد ، كما دل عليه طيف الأشعة تحت الحمراء وطيف الرنين النووي المغناطيسي في وضع ترانس لذرة النيتروجين المانحة . ووجد أن الانزياح الكيميائي لذرة الكربون -١٣ (C-7) لهذه المعقّدات كان عند 235-238ppm في حين أنه كان عند 160-170ppm لذرة كربون الإيمين (C-7').