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Journal of Organometallic Chemistry 593–594 (2000) 226–231

Journal of Organometallic Chemistry

Conformational constraints and σ–π-vinyl interchange in μ_3-η^3-5,6-dihydroquinoline triosmium complexes

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Received 4 June 1999; accepted 27 October 1999

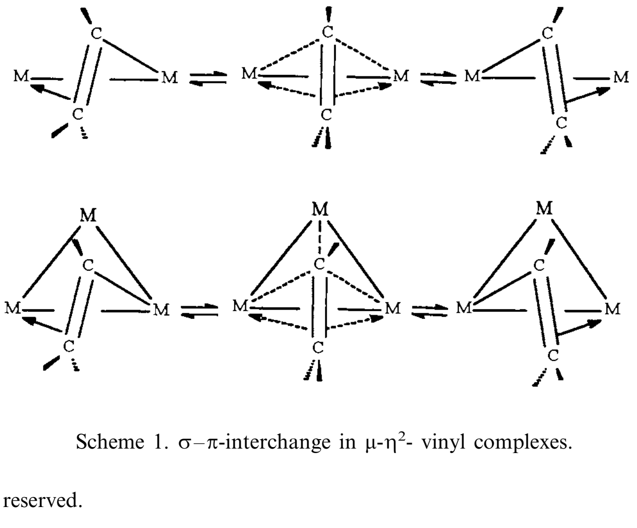
Abstract

The rates of the σ–π-interchange processes in the series of 5,6-dihydro-μ_3-η^3-quinolyl complexes $Os_3(CO)_9(C_9H_6(5\text{-}R,6\text{-}R')N)(\mu\text{-}H)$ ($R = R' = H$, **1**, $R = {}^nBu$, $R' = H$, **2**; R = allyl, $R' = CH_3$, **3**, $R = C(CH_3)_2CN$, $R' = CH_3$, **4**; $R = –CHS(CH_2)_2S–$, $R' = CH_3$, **5**; $R = CH_2CO_2^tBu$, $R' = CH_3$, **6**; $R = CH_2CO_2^tBu$, $R' = Cl$, **7**) have been examined by ^{1}H-NMR spectroscopy using the ^{187}Os–^{1}H satellites as a dynamical probe. It was found that the unsubstituted and monosubstituted derivatives **1** and **2** are dynamic with respect to the σ-π-interchange process throughout the temperature range examined (+25 to −80°C). The disubstituted derivatives **3**–**6** on the other hand are rigid on the NMR time scale up to +100°C where coalescence of the satellites is observed. For compound **7**, the barrier to σ–π-interchange is intermediate between **1** and **2** and **3**–**6**, exhibiting coalescence at +70°C. Compound **7** also exhibits evidence for population of a second isomer as observed from VT ^{1}H-NMR of the vinylic proton. The results are discussed in the context of the conformational constraints around the 5,6-carbon–carbon bond of the carbocyclic ring in these dihydroquinolyl complexes and are compared with previously reported σ–π-vinyl interchange processes. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Conformational constraints; Vinyl interchange; Triosmium complexes

1. Introduction

The σ–π-vinyl interchange process is observed to be rapid on the NMR time scale in most μ-η^2-σ–π-vinyl di- and trimetallic complexes at ambient temperatures (Scheme 1) [1–7]. The process does not require formal bond dissociation of either the σ- or π-bond from the metal, but rather a concerted motion in which the face of the olefin bound to the metal is changed by shifting to the other metal of the binuclear moiety while the σ-bond passes through a μ-alkylidene intermediate (Scheme 1). In the case of trimetallic complexes, a μ_3-involvement of the σ-bound carbon is suggested by the observation of ^{13}C–^{13}C coupling between this carbon and carbonyl groups on the unique osmium atom (Scheme 1) [6]. The non-involvement of formal bond cleavage is also suggested by the fact that upon thermolysis dissociation of the σ–π-vinyl ligand is not observed; rather, elimination of H_2 and conversion to μ-η^2- or μ_3-η^2-acetylide complexes is the observed reaction pathway [6,8]. The barrier to σ–π-vinyl interchange (43–47 kJ mol^{-1}) [3–7] is not very sensitive to



Scheme 1. σ–π-interchange in μ-η^2- vinyl complexes.

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PII: S0022-328X(99)00661-0

the substituents on the vinyl group, but phosphine substitution on the cluster leads to unequal isomer populations [4]. Bulkier phosphines favor the remote isomer where the phosphine is on the osmium atom not involved in bonding with the vinyl moiety, while with less bulky phosphines the isomer which has the σ-bond of vinyl group coordinated to the phosphine substituted osmium atom is favored [4]. A third isomer in which the vinyl group is π-bound to the phosphine substituted osmium atom was proposed to be present in undetectable amounts (by ^{13}C-NMR) and to be in rapid exchange with its σ–π-interchange isomer based on variable temperature studies [4].

We recently reported a new type of σ–π-vinyl complex which results from the nucleophilic addition–acid quench of the electron deficient quinoline complexes of general formula $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_9H_5(6\text{-}R')N)(\mu\text{-}H)$ ($R' = H$, alkyl, alkoxy, amino) (Eq. 1) [9,10]. The parent quinoline complex ($R' = H$) undergoes a σ–π-vinyl interchange with an activation energy of 41 ± 2 kJ mol^{-1}. The corresponding mono- and disubstituted derivatives have not been examined with regard to the rate of the σ–π-vinyl interchange process. The unusual conformations adopted by the disubstituted derivatives in the solid state suggested that the rate of the σ–π-vinyl interchange might be affected [10]. Given the stereoselective nature of these nucleophilic addition reactions, we are very interested in devising methodologies for cleaving the nucleophilic addition products from the cluster [10]. The rigidity of the organic framework in these clusters may or may not be related to the energetics of the desired cleavage reaction. The usual means of determining the rate of the σ–π-vinyl interchange in metal carbonyl complexes is to observe the variable temperature (VT) ^{13}C-NMR of the carbonyl carbons on the metal atoms bound to the σ–π-vinyl moiety [1–7,9]. At the low temperature limit the environments at the metal atoms bridged by the vinyl ligand are different. The onset of the σ–π-vinyl interchange averages these environments and the barrier to this process can be estimated by evaluating the pairwise exchange rates of the carbonyl groups on the vinyl bound metal atoms [9]. Unfortunately, in the mono- and disubstituted μ_3-η^3-5,6-dihydroquinoline complexes (Eq. 1), the chiral centers at C(5) and/or C(6) render the bridged metal atoms magnetically non-equivalent even when the σ–π-vinyl interchange process is rapid on the NMR time scale. Another possible way to probe the rate of the σ–π-vinyl exchange process is to examine the ^{187}Os–^{1}H satellites (^{187}Os natural abundance = 1.64%). Here, we only observe molecules with one or no ^{187}Os isotopes in the cluster owing to its low natural abundance [11]. When σ–π-vinyl interchange is slow on the NMR time scale there will be two isotopomers; one group of clusters with an ^{187}Os bound to the vinyl group with a σ-bond and the second set of clusters with a single ^{187}Os and a π-bond to the vinyl moiety; two sets of satellites will be then observed. As the σ–π-vinyl interchange process becomes rapid on the NMR time scale these satellites will merge to a single set with a value which will be the average of the two values observed in the limit of slow exchange as long as the hydride remains static on the NMR time scale. This approach gets around the inherent asymmetry in the quinolyl complexes which have a substituent in the 5- or 6-position. By monitoring the σ–π-vinyl interchange at one Os atom per isotopomer it is not required that the two osmium atoms become magnetically equivalent for the process to be averaged on the NMR time scale but only that a single Os atom sees an averaged environment. We report here the results of our observations on the variable temperature behavior of the ^1J ^{187}Os–^{1}H satellites for a series of mono- and disubstituted 5,6-dihydro-μ_3-η^3-quinolyl triosmium clusters which reveal a considerable sensitivity of the σ–π-vinyl exchange process to the substituents on the 5- and 6-positions of the carbocyclic ring.

2. Results and discussion

The ^{187}Os–^{1}H satellites for the parent complex $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_6N)(\mu\text{-}H)$ (**1**) and the monosubstituted derivative $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_5(5\text{-}^nBu)N)(\mu\text{-}H)$ (**2**) both appear as a single set with values of 33.3 and 32.8 ± 0.3 Hz, respectively (Fig. 1 and Table 1). This indicates that the σ–π-vinyl exchange process is rapid on the NMR time scale. This remains the case down to −80°C, the temperature at which σ–π-vinyl interchange is moderately slow on the NMR time scale with respect to averaging of the carbonyl resonances. Based on the observed $\Delta G^{\ddagger}$ for this process in **1** (41.0 ± 2 kJ mol^{-1}) we estimate that given a chemical shift difference of about 4 Hz in the satellites at the low temperature limit (vide infra and Table 1) of the σ–π-vinyl exchange a coalescence temperature of −90°C would be sufficient to average the satellites, consistent with the observation of a single set of satellites at −80°C [9]. We can conclude therefore that the $\Delta G^{\ddagger}$ for **2** is about the same as for **1**.

In sharp contrast, the disubstituted derivatives *cis*-$Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_4(5\text{-}R)(6\text{-}R')N)\text{-}(\mu\text{-}H)$ ($R = CH_2CHCH_2$, $R' = CH_3$, **3**; $R = (CH_3)_2CCN$, $R' = CH_3$, **4**; $R = \text{–}CHS(CH_2)_2S\text{–}$, $R' = CH_3$; **5**, $R = CH_2CO_2^tBu$, $R' = CH_3$; **6**) which are all isolated as a single *cis*-diastereomer [10] exhibit two sets of ^{187}Os–^{1}H satellites with one set having values between 30.7 and 31.1 ± 0.3 Hz and the other between 35.1 and 35.2 ± 0.3 Hz. These values are all in the range previously observed for static hydrides in triosmium clusters [11]. This indicates that the rate of σ–π-vinyl interchange is slow on the NMR time scale (Table 1, Fig. 1). Even though

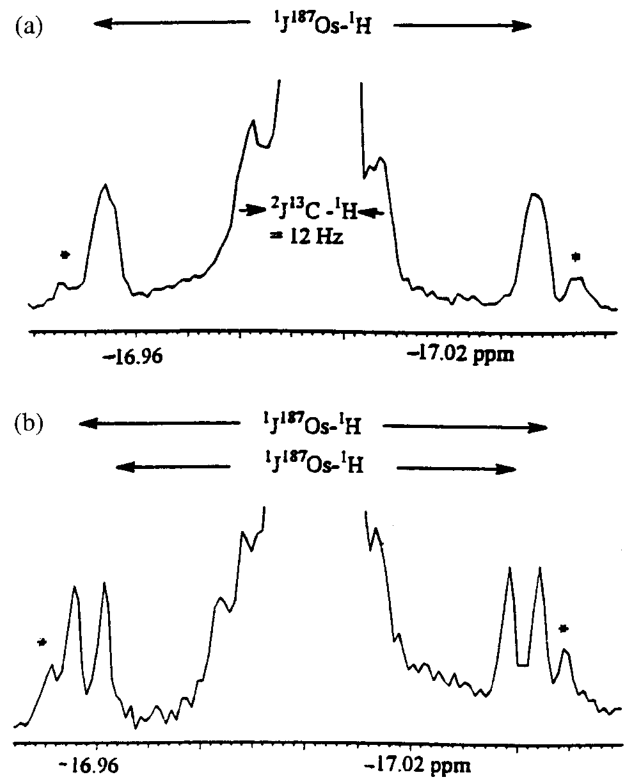


Fig. 1. (a) ^{1}H-NMR of the hydride region of $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_5(5\text{-}{}^nBu)N)(\mu\text{-}H)$ (**2**) at ambient temperature. (b) ^{1}H-NMR of the hydride region of $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_4(5\text{-}SCHS(CH_2)_26\text{-}CH_3)N)(\mu\text{-}H)$ (**5**) at ambient temperature. * = spinning side bands.

these complexes are formed as a single diastereomer there still exists the possibility that different conformers could be populated owing to the flexibility of the 5,6-bond of the carbocyclic ring. That only two sets of satellites are observed indicates that only one rigid conformer is populated or that there is fortuitous overlap between populated conformers in these 5,6-disubstituted σ–π-vinyl complexes. Indeed, the fact that the rate of σ–π-vinyl interchange is slow on the NMR time scale for **1** and **2** supports the idea that steric crowding around the 5,6-bond restricts the flexibility of the carbocyclic ring. Inspection of molecular models based on the solid-state structure of **4** reveal that the bulky isobutyryl nitrile group at the 6-position blocks axial–radial interconversion at the 5-position and therefore locks the *cis*-diastereomer into one conformer [10]. We attempted to examine the 5,6-dimethyl derivative to see if it was sufficient to have two small groups in the 5- and 6-positions in order to lock the conformation of the carbocyclic ring. Unfortunately, this compound was contaminated with small amounts of the corresponding inseparable *trans*-diastereomer (5–10%) whose hydride resonance, side bands and satellites overlapped with the satellites of interest making assignment of the satellites difficult and any conclusions unreliable [10].

On heating samples of **3**–**6** in toluene at 100°C, we observed coalescence of the double satellites to a single broad peak (Fig. 2). The base of the central hydride peak is also broadened due to the averaging of the [2]J ^{13}CO–^{1}H satellites. However, the ^{187}Os–^{1}H satellite peak maxima can be discerned and gives average values in excellent agreement with those calculated from the ambient temperature data (Table 1, Fig. 2). If we assume a coalescence temperature of 100°C and treat the difference in the ^{187}Os–^{1}H coupling constants as a chemical shift difference, we can estimate the average $\Delta G^{\ddagger}$ for the σ–π-vinyl interchange to be 85 ± 2 kJ mol^{-1} at 100°C. For this intramolecular process, contributions from $\Delta S^{\ddagger}$ would be expected to be small and thus we can compare this number with the 41.0 ± 2 kJ mol^{-1} observed for **1** and conclude that substitution at both the 5- and 6-positions in these μ_3-η^3-dihydroquinoline complexes has a profound influence on processes occurring at the metal core–ligand interface.

Compound **7** ($R = CH_2CO_2^tBu$, $R' = Cl$) is unique among the series examined in that it appears that a second conformer is populated at a level where the individual signals are not detectable by ^{1}H-NMR at 400 MHz. This is evident from the appearance of the proton resonance at 3.51 ppm, which appears as a broad-

Table 1
^{187}Os-hydride coupling constants (Hz) [a,b]

Compound	Hydride (δ)	R_5	R_6	$J_{Os\text{–}H}$ inner	$J_{Os\text{–}H}$ outer	Average
1	−16.82	H	H			33.3
2 [c]	−16.98	^{n}Bu	H			32.8
3	−17.03	CH_2CHCH_2	CH_3	31.1	35.2	33.1
4	−17.00	$C(CH_3)_2CN$	CH_3	30.7	35.4	33.0
5 [c]	−16.92	$-CHS(CH_2)_2S-$	CH_3	30.7	35.2	32.9
6	−17.09	$CH_2CO_2^tBu$	CH_3	31.0	35.1	33.1
7	−17.33	$CH_2CO_2^tBu$	Cl	32.0	30.8	31.4
Average of (**1**–**7**)						32.7

[a] ±0.3 Hz.
[b] Spectra taken in toluene-d_8 unless otherwise noted.
[c] Spectra taken in $CDCl_3$.

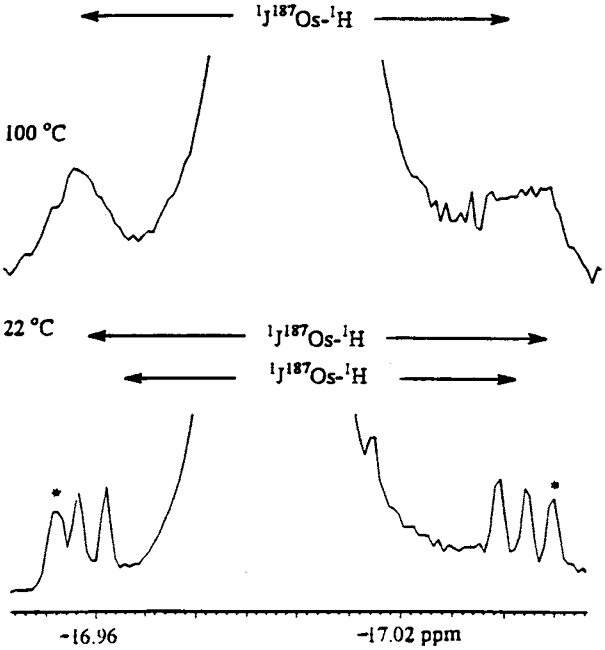


Fig. 2. ^{1}H-NMR of the hydride region of $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_4(5\text{-}C(CH_3)_2CN, 6\text{-}CH_3)N)(\mu\text{-}H)$ (**4**) at ambient temperature and 100°C. * = spinning side bands.

ened singlet at ambient temperatures. This resonance is assigned to the vinylic proton on C(7) of the carbocyclic ring (2D-^{1}H COSY) [10]. As the temperature is decreased to −45°C, this resonance sharpens to a doublet and shifts upfield (Fig. 3). Increasing the temperature to +55°C results in a sharpening of the broadened singlet observed at ambient temperatures to a doublet and a downfield shift. The behavior of this resonance is consistent with the existence of a second isomer or conformer, present at levels not detectable by ^{1}H-NMR at 400 MHz, with proton chemical shifts very similar to the major isomer except for the vinylic proton on C(7). This interpretation is supported by ^{1}H-NMR measurements at 600 MHz where a small broad hydride resonance is observed at −17.07 ppm at −40°C which averages with the major hydride resonance at −17.33 ppm as the temperature is increased (Fig. 4). A broad resonance is observed at 4.50 ppm which averages with the resonance assigned to H(7) observed at 3.57 ppm at −40°C. Both of these companion resonances integrate to about 5% relative to the major resonances (Fig. 4). Taking the weighted average of the H(7) resonances gives a value of 3.62 ppm, in excellent agreement with the observed chemical shift for this resonance (3.63 ppm, Fig. 3). The population ratio of 19:1 used in this calculation does not take into account the population increase in the minor isomer that would be expected on going from −40 to +55°C. Assuming that the entropy change would be close to zero for this process the conformer ratio would be about 9:1 at +55°C which gives a weighted average chemical shift of 3.66 ppm still in reasonable agreement with the observed shift for H(7). We propose that the two species are interconverted by the σ–π-vinyl interchange process and differ from each other by the conformational disposition of the chlorine atom on C(6) relative to the proton on C(7) and brought about by a ring flip at the C(5)–C(6) bond (Scheme 2). That the interconversion of these conformers is brought about by the σ–π-vinyl interchange is supported by the fact that the pair of ^{187}Os–^{1}H satellites observed for **7** are significantly broadened at room temperature (r.t.) and exhibit a smaller difference in magnitude than **3**–**6** (Table 1). These broadened satellites average to a single broadened set of satellites at +70°C, a much lower temperature than that observed for **3**–**6** (Fig. 5). The $\Delta G^{\ddagger}$ for the σ–π-vinyl interchange in **7** is estimated to be 78 ± 2 kJ mol^{-1}. The population of this second conformer and the lower barrier to σ–π-vinyl interchange in **7** can be rationalized by a destabilization of the ground state of the major conformer brought about by the presence of the bulkier chlorine atom on C(6) in **7** (relative to the methyl groups in **3**–**6**) along with a large cone swept out by the *t*-butylacetate group on C(5). Thus, this behavior is not observed in **6** or in the previously reported 6-chloro-5-isobutyryl nitrile dihydroquinoline complex [10]. These results confirm that the conformational flexibility of the carbocyclic ring at the 5,6-bond of the carbocyclic ring has a strong influence on the rate of the σ–π-vinyl interchange process

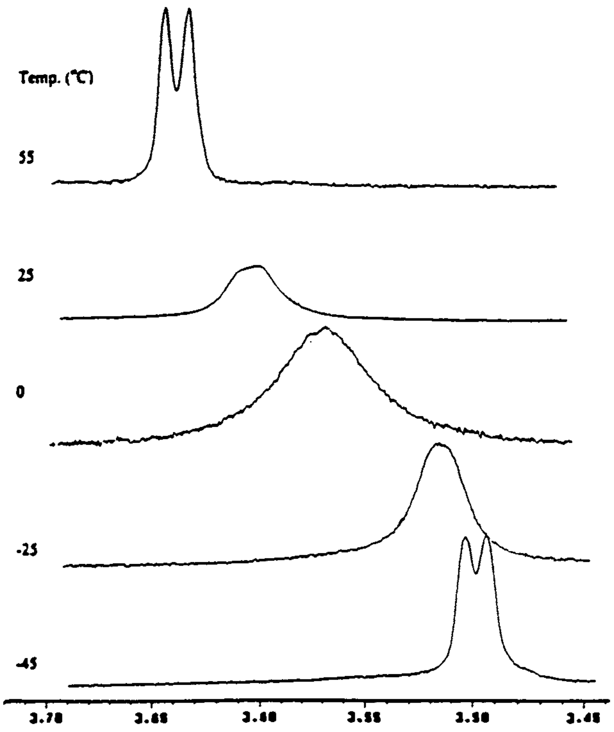


Fig. 3. Variable temperature ^{1}H-NMR of $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_4(5\text{-}CH_2CO_2^tBu, 6\text{-}Cl)N)(\mu\text{-}H)$ (**7**) showing the vinylic proton.

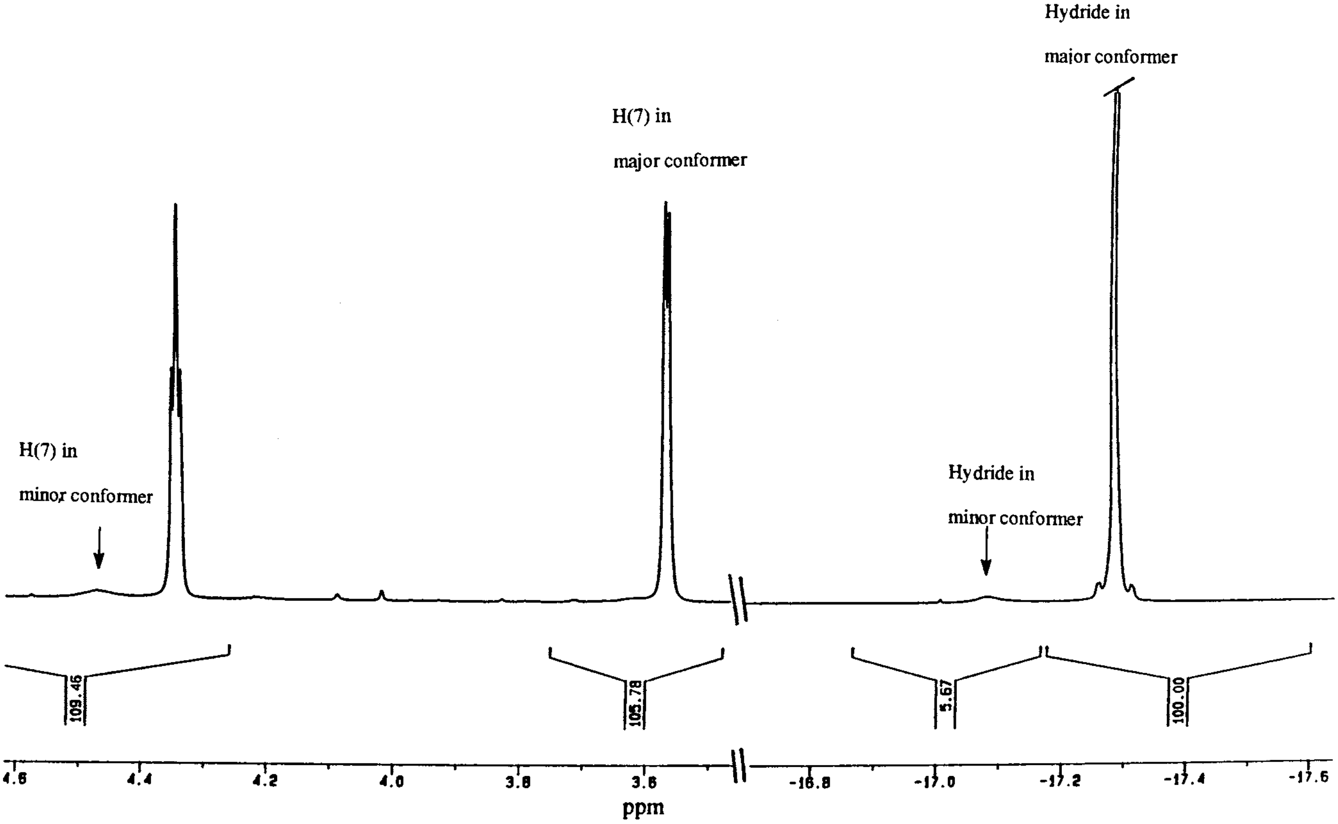


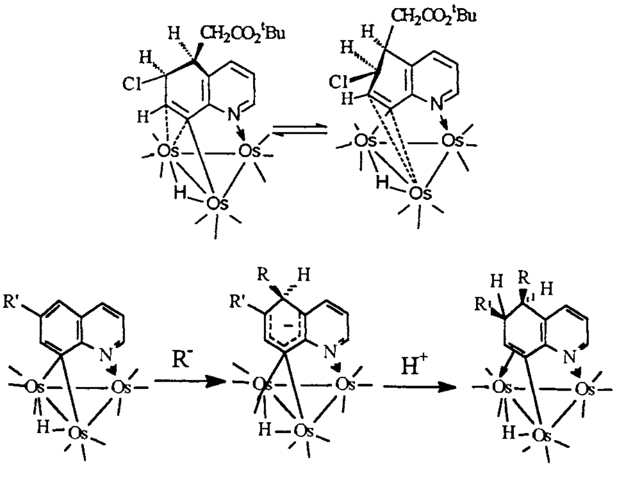
Fig. 4. ^{1}H-NMR of $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_4(5\text{-}CH_2CO_2^tBu, 6\text{-}Cl)N)(\mu\text{-}H)$ (**7**) in the vinylic and hydride regions at 600 MHz, at −40°C.

and that **3**–**6** exist as a single conformer in solution as well as in the solid state. The detection of a second low abundance conformer for compound **7** is reminiscent of the work of Shapley et al. where a second undetectable isomer (by ^{13}C-NMR) is observed in $Os_3(CO)_9(\mu\text{-}\eta^2\text{-}CH{=}CH_2)(\mu\text{-}H)PPh_3$ [4]. The major isomer has a σ-bond to an $Os(CO)_3$ group and a π-bond to an $Os(CO)_2PPh_3$ group. The minor 'unseen' isomer has the opposite configuration and variable temperature and spin saturation transfer experiments lead to the conclusion that the two isomers are involved in a σ–π-vinyl interchange process.

We are currently exploring the impact that slowing down the σ–π-vinyl interchange process has on the stereochemistry of nucleophilic attack on (C7) in this series of complexes.

3. Experimental

Compounds **1**–**5** and **7** were prepared according to published literature procedures [9,10]. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl before use. The ^{n}BuLi used to prepare the $CH_2CO_2^tBu$ carbanion [10] was purchased from Aldrich and the di-isopropyl amine (Aldrich) was distilled from calcium hydride before use. NMR solvents, toluene-d_8 and dichloromethane-d_2 (Cambridge Isotopes) were ordered in sealed ampules and used as received; $CDCl_3$ (Aldrich) was dried over molecular sieves. NMR spectra were obtained on a Varian Unity Plus 400 or a Bruker 600 MHz Avance spectrometer and IR spectra were obtained on a Perkin–Elmer 1600 FT-IR spectrometer. Chemical shifts were referenced internally relative to the residual protons in the deuterated solvents used. Temperatures are reported to ± 1°C based on calibration with a methanol standard. Elemental



Scheme 2. Confomers of **7**.

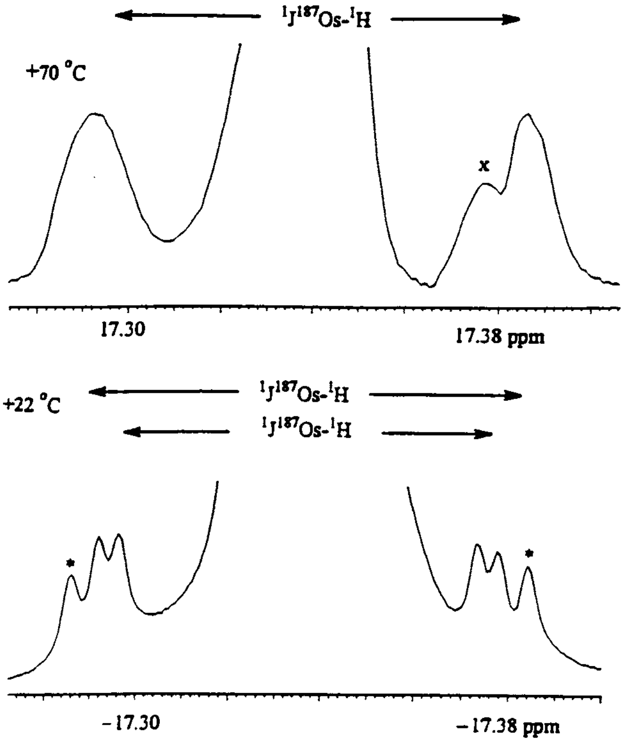


Fig. 5. ^{1}H-NMR of the hydride region of $Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_9H_4(5\text{-}CH_2CO^tBu, \text{-}6\text{-}Cl)N)(\mu\text{-}H)$ (**7**). * = spinning side bands x = impurity.

analyses were performed by Schwarzkopf Microanalytical Labs, Woodside, NY. Free energies of activation were estimated using the formula $\Delta G^{\ddagger}$ (kJ mol^{-1}) = $T_c 19.14 \times 10^{-3}(\log T_c/\Delta\nu + 9.975)$ [12].

3.1. Preparation of $Os_3(CO)_9(\mu^3\text{-}\eta^3\text{-}C_9H_6\text{-}(5\text{-}CH_2CO_2^tBu, 6\text{-}CH_3)N)(\mu\text{-}H)$ (6)

$Os_3(CO)_9(\mu^3\text{-}\eta^2\text{-}C_9H_5(6\text{-}CH_3)N)(\mu\text{-}H)$ [9] (75 mg, 0.078 mmol) was dissolved in 5 ml of THF and cooled to − 78°C, at which time a 3 M excess of the $LiCH_2CO_2^tBu$ carbanion [10] was slowly added by syringe. The reaction mixture was warmed to 0°C, stirred for 1 h, then cooled again to − 78°C and quenched with trifluoroacetic acid (0.34 mmol, 10% in excess of the carbanion added). The solution turned orange as it warmed to room temperature. The solution was then rotary evaporated, taken up in a minimum amount of CH_2Cl_2, filtered, and purified by TLC on a 0.1 × 20 × 20 cm silica gel plate using 20% CH_2Cl_2 in hexanes. One major orange band containing the product was observed in addition to a smaller band of starting material and a minor band of rearomatized product. Yield: mg, 53.2%. Anal. Calc. for $C_{25}H_{21}NO_{11}Os_3$: C, 27.75; H, 1.96; N, 1.29. Found: C, 27.87; H, 2.03; N, 1.34%. IR (ν CO in hexanes): 2082 (m), 2050 (s), 2030 (s), 2007 (m), 1994 (s), 1973 (w), 1966 (w), 1955 (w) cm^{-1}. ^{1}H-NMR in $CDCl_3$: δ 8.430 (dd, H(2)), 7.495 (dd, H(4)), 6.796 (dd, H(3)), 3.472 (d, H(7)), 2.947 (m, H(5)), 2.495 (dd, CH_2, 1H), 2.388 (m, H(6)), 2.306 (dd, CH_2, 1H), 1.334 (s, CH_3, 9H), 1.276 (s, CH_3), − 17.089 (s, hydride).

Acknowledgements

We gratefully acknowledge the National Science Foundation (Grant #CHE9625367, E. Rosenberg), the Consiglio Nazionale delle Ricerche (CNR, L. Milone), the CNR Programma di Scambi Internazionali (E. Rosenberg) and the NATO Science Program (E. Rosenberg and L. Milone).

References

[1] J.B. Keister, J.R. Shapley, J. Organomet. Chem. 85 (1975) C22.
[2] J.R. Shapley, S.I. Richter, M. Tachikawa, J.B. Keister, J. Organomet. Chem. 94 (1975) C43.
[3] A.D. Clauss, M. Tachikawa, J.R. Shapley, C.G. Pierpoint, Inorg. Chem. 20 (1981) 1528.
[4] D.H. Hamilton, J.R. Shapley, S.R. Wilson, M. Koike, Organometallics 15 (1996) 4930.
[5] H. Hamilton, J.R. Shapley, Organometallics 17 (1998) 3087.
[6] S. Aime, R. Gobetto, D. Osella, L. Milone, E. Rosenberg, E. Anslyn, Inorg. Chim. Acta 111 (1986) 95.
[7] L.J. Farrugia, Y. Chi, W.C. Tu, Organometallics 12 (1993) 1616.
[8] E. Rosenberg, E. Anslyn, S. Aime, L. Milone, R. Gobetto, D. Osella, Gaz. Chim. Ital. 118 (1988) 299.
[9] E. Arcia, D.S. Kolwaite, E. Rosenberg, K. Hardcastle, J. Ciurash, R. Duque, R. Gobetto, L. Milone, D. Osella, M. Botta, W. Dastru', A. Viale, J. Fiedler, Organometallics 17 (1998) 415.
[10] B. Bergman, R. Holmquist, R. Smith, E. Rosenberg, K.I. Hardcastle, M. Visi, J. Ciurash, J. Am. Chem. Soc. 120 (1998) 12818.
[11] L.J. Farrugia, Organometallics 8 (1989) 2410.
[12] I.O. Sutherland, in: E.F. Mooney (Ed.), Annual Reports in NMR Spectroscopy, vol. 4, Academic Press, New York, 1971, pp. 71–235.