ORGANOMETALLICS

Studies on the fluxional behavior of the tetrahedro-triosmium-platinum clusters Os3Pt(.mu.-H)2(CO)9(PCy3)(CNCy) and Os3Pt(.mu.-H)2(.mu.-CH2)(CO)9(PCy3)(CNCy) using carbon-13 EXSY. Direct evidence for the rotation of the Pt(H)(PCy3)(CNCy) unit from dynamic osmium-187-hydride coupling constants

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Studies on the Fluxional Behavior of the *tetrahedro*-Triosmium–Platinum Clusters $Os_3Pt(\mu\text{-}H)_2(CO)_9(PCy_3)(CNCy)$ and $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_9(PCy_3)(CNCy)$ Using ^{13}C EXSY. Direct Evidence for the Rotation of the Pt(H)(PCy$_3$)(CNCy) Unit from Dynamic ^{187}Os–Hydride Coupling Constants

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The hydride ligands in $Os_3Pt(\mu\text{-}H)_2(CO)_9(PCy_3)(CNCy)$ undergo slow exchange at 298 K, although examination of the temperature variation of $J(^{187}Os\text{–}H)$ reveals a rapid fluxional process corresponding to mutual exchange between the isotopomers of the $^{187}OsOs_2Pt$ species, with an estimated $\Delta G^{\ddagger}$ of 56 (±1) kJ mol^{-1}. The proposed mechanism involves the rotation of the Pt(H)(PCy$_3$)(CNCy) group about the Os$_3$ triangle, coupled with a conrotary migration of the Os(μ-H)Os hydride to an adjacent Os–Os edge. The 1D and 2D EXSY ^{13}C NMR spectra reveal two CO exchange processes, a lower energy tripodal rotation in the two equivalent Os(CO)$_3$ groups ($\Delta G^{\ddagger}_{200}$ = 51.7 (±1.0) kJ mol^{-1}) and a higher energy process, commensurate with the hydride mobility, which completely scrambles all CO ligands ($\Delta G^{\ddagger}_{225}$ = 58.7 (±1.3) kJ mol^{-1}). Variable-temperature ^1H and ^{13}C NMR studies on $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_9(PCy_3)(CNCy)$ provide no direct evidence for rotation of the PtL$_3$ group but show a slow exchange of the hydrides ($\Delta G^{\ddagger}_{373}$ = 85.6 (±0.8) kJ mol^{-1}). 2D EXSY ^{13}C NMR spectra reveal three CO exchange processes; separate tripodal rotations of two of the Os(CO)$_3$ groups ($\Delta G^{\ddagger}_{318}$ = 80.5 (±1.0) and 88.4 (±1.6) kJ mol^{-1}) and the racemization of the cluster by hydride migration ($\Delta G^{\ddagger}_{318}$ = 84.7 (±1.1) kJ mol^{-1}).

Introduction

The relative ease with which intramolecular ligand migrations occur in metal clusters was recognized at an early stage,[1,2] and interest in this fundamental physicochemical property remains high.[3] Studies on the energetics and mechanisms of fluxional processes provide information about thermally accessible excited-state molecular geometries, which in turn may have relevance to the intermediates involved in catalytic conversions at heterogeneous surfaces. Both metal-localized and intermetal ligand exchanges are common,[1,2] and these processes are sometimes accompanied by metal framework rearrangements.[4,5] Barriers to metal-localized exchange may be amenable to theoretical analysis by approximate MO methods.[6] In such a study Hoffmann and Schilling[7] have predicted a low (~25 kJ mol^{-1}) barrier to rotation of the PtL$_2$ unit in clusters of the type $[\{L_2Pt\}M_3(CO)_9]^{2-}$. With a view to observing such behavior in triosmium–platinum clusters, we have investigated[8] the fluxionality of $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)$ (**1**) and $[Os_3Pt(\mu\text{-}H)_3(CO)_{10}(PCy_3)]^+$ (**2**). Both these clusters show fluxional behavior which is compatible with the rotation of the PtL$_2$ (or PtL$_2$(H)[9]) unit, although other processes such as a "merry-go-round" CO exchange cannot be excluded. Herein are described NMR studies on the related isocyanide-substituted clusters $Os_3Pt(\mu\text{-}H)_2(CO)_9(PCy_3)(CNCy)$ (**3**) and $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_9(PCy_3)(CNCy)$ (**4**),[10] which provide direct evidence, from dynamic ^{187}Os–hydride couplings, for the rotation of the Pt(H)(PCy$_3$)(CNCy) unit in **3**.

Table I. NMR Parameters for $Os_3Pt(\mu\text{-}H)_2(CO)_9(PCy_3)(CNCy)$ (3)

reson	chem shift/ppm	mult[a]	J/Hz Pt	J/Hz P	J/Hz H1	J/Hz H2
		^{13}C Data[b,c]				
a	192.8	s (2)	30			3.2
b	184.8	s (2)	16		4.2	
c	182.1	s (2)	36		11.8	
d	180.9	s (1)	50			7.8
e	180.2	d (2)		7.0	3.1	
CyNC	117.0	s (1)	1468[d]			
		^1H Data[c,e]				
H1	−8.19	s (1)	6.5			
H2	−11.42	d (1)	544	9.1		

[a] Multiplicities in ^{13}C spectra based on ^1H-decoupled spectra. [b] 213 K, CD$_2$Cl$_2$. [c] Ppm relative to TMS. [d] ^{195}Pt coupling observed in spectrum recorded at ambient temperature. [e] 233 K, CDCl$_3$.

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[1] Johnson, B. F. G.; Benfield, R. E. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: Chichester, 1980; pp 471–543.

[2] Band, E.; Muetterties, E. L. *Chem. Rev.* **1978**, *78*, 639.

[3] For recent examples of cluster fluxionality see: (a) Clark, D. T.; Sutin, K. A.; McGlinchey, M. J. *Organometallics* **1989**, *8*, 155. (b) Allevi, C.; Bordoni, S.; Clavering, C. P.; Heaton, B. T.; Iggo, J. A.; Seregni, C.; Garlaschelli, L. *Ibid.* **1989**, *8*, 385. (c) Hajela, S.; Novak, B. M.; Rosenberg, E. *Ibid.* **1989**, *8*, 468. (d) Deeming, A. J.; Kabir, S. E.; Nuel, D.; Powell, N. I. *Ibid.* **1989**, *8*, 717. (e) Fumagalli, A.; Pergola, R. D.; Bonacina, F.; Garlaschelli, L.; Moret, M.; Sironi, A. *J. Am. Chem. Soc.* **1989**, *111*, 165. (f) Boyar, E.; Deeming, A. J.; Felix, M. S. B.; Kabir, S. E.; Adatia, T.; Bhusate, R.; McPartlin, M.; Powell, H. R. *J. Chem. Soc., Dalton Trans.* **1989**, 5. (g) Pursiainen, J.; Pakkanen, T. A. *J. Organomet. Chem.* **1989**, *362*, 375.

[4] Salter, I. D. *Adv. Dynamic Stereochem.* **1989**, *2*, in press.

[5] For some examples of metal core rearrangements in tetranuclear clusters see: (a) Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics* **1988**, *7*, 294. (b) Adams, R. D.; Horvath, I. T.; Wang, S. *Inorg. Chem.* **1986**, *25*, 1617. (c) Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *Inorg. Chem.* **1984**, *23*, 4476.

[6] (a) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801. (b) Barr, R. D.; Green, M.; Howard, J. A. K.; Marder, T. B.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 2757.

[7] Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456.

[8] Ewing, P.; Farrugia, L. J.; Rycroft, D. S. *Organometallics* **1988**, *7*, 859.

[9] The presence of the hydride does not unduly perturb the lobal properties of the frontier orbitals of the PtL$_2$ unit, though of course Pt(μ-H)M rather than Pt–M bonds result from the interaction with the M$_3$(CO)$_9$ cluster unit.

[10] Ewing, P.; Farrugia, L. J. *Organometallics* **1988**, *7*, 871.

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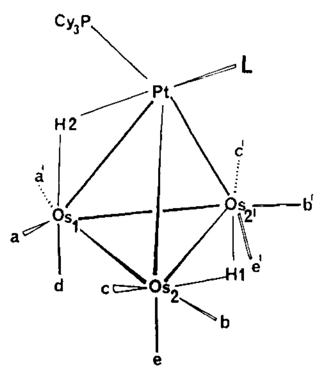
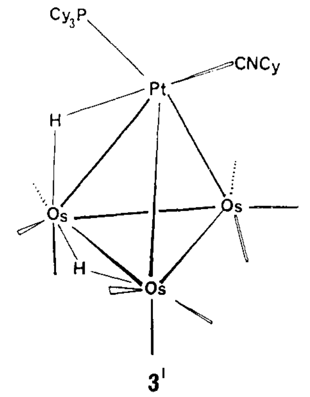


1; L=CO **3**; L=CNCy



3'

Results and Discussion

Hydride Fluxionality in 3. The ^{1}H NMR spectrum of **3** displays two signals in the hydride region at δ −8.19 and −11.42, which on the basis of ^{195}Pt couplings (Table I) may be assigned to the Os(μ-H)Os and Os(μ-H)Pt protons H1 and H2, respectively. These resonances show no exchange broadening at 298 K ($\Delta\nu_{1/2} \sim 2$ Hz), though magnetization transfer studies indicate a slow mutual exchange.[11] By contrast, the closely related complex **1** shows substantial broadening at this temperature due to the exchange of the hydride sites ($\Delta G^{\ddagger}_{295}$ = 63.1 (±0.5) kJ mol^{-1}).[8] Replacement of the Pt–CO ligand in **1** by a Pt–CNCy group in **3** thus raises the exchange barrier considerably. Keister and Shapley[13] have also shown that the H–H exchange barrier for L = CNR is greater than for L = CO in the clusters $Os_3(\mu\text{-H})(H)(CO)_{10}(L)$. The known trans influence of CNR compared with CO[14] should lead to a *weaker* Pt–H bond in **3**, and the values of ^1J(Pt–H) bear this out (590 Hz in **1**[8] and 544 Hz in **3**). Other factors must thus be responsible for this effect.

Both hydride signals display low-intensity satellites due to coupling to ^{187}Os ($I = {}^1/_2$, natural abundance 1.64%), and examination of the temperature dependence of these couplings (shown in Figure 1 at the fast- (298 K) and slow- (238 K) exchange regimes) reveals a "hidden" fluxional process. Due to the low natural abundance of ^{187}Os, we only observe those isotopomers containing either none or one ^{187}Os nucleus, and the satellite subspectra thus arise from the three isotopomers (i), (i′), and (ii) shown in Scheme I. The ^{187}Os coupling to H1 is reduced from 41.8 Hz at 238 K to 27.3 Hz at 298 K, while to H2 it is reduced[15] from 31.4 to 9.7 Hz. The satellites for H2 at 298 K (Figure 1b) appear as a pseudotriplet due to the similarity between $J_{av}(^{187}\text{Os–H})$ = 9.7 Hz and J(P–H) = 9.1 Hz. Values for *static* $^1J(^{187}\text{Os–H})$ coupling constants have been reported for a number of Os clusters,[12a,16] and they usually fall in the range 25–35 Hz, although in unsaturated clusters they may be slightly greater.[8,12a,16c] The couplings observed at

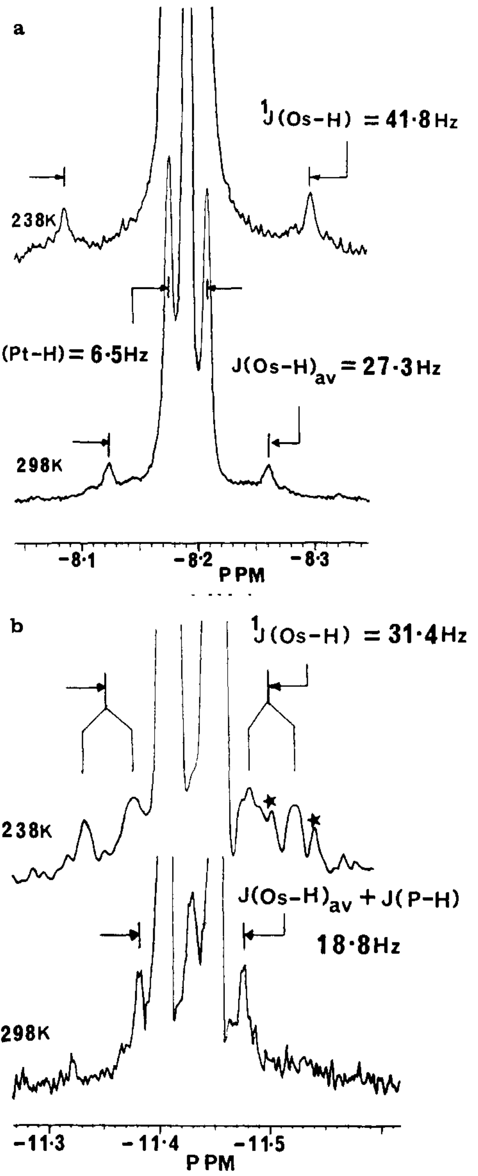
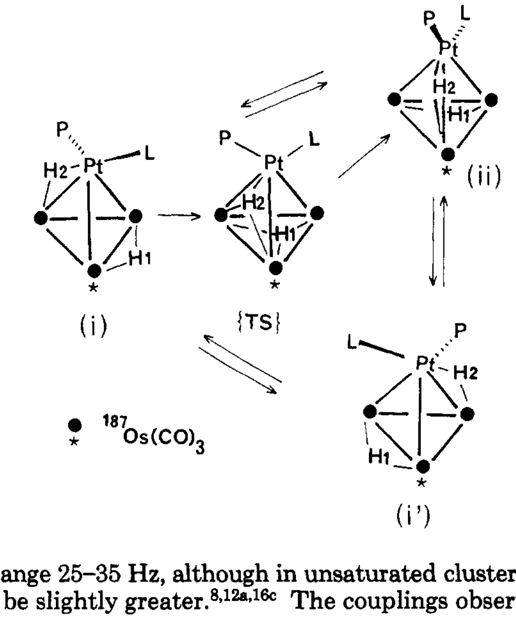


Figure 1. The ^{187}Os satellites on the high field ^{1}H NMR signals of complex **3** at 238 and 298 K for (a) the Os(μ-H)Os hydride and (b) the Os(μ-H)Pt hydride. The asterisk indicates an impurity.

Scheme I



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[11] Saturation of the signal at δ −8.19 resulted in partial saturation at δ −11.42. Due to the expected interhydride NOE's (see ref 8 and 12) a quantitative magnetization transfer study was not undertaken. From the line width at 333 K a *lower* limit of ca. 74 kJ mol^{-1} for the hydride exchange is estimated, using the approximation $k = \pi\Delta\nu_{1/2}$. Differential η's are expected for the two hydrides; cf. T_1 values of 0.9 and 3.6 s were measured for the Os(μ-H)Pt and Os(μ-H)Os protons, respectively.

[12] (a) Willis, A. C.; Einstein, F. W. B.; Ramadan, R. M.; Pomeroy, R. K. *Organometallics* **1983**, *2*, 935. (b) Ma, A. K.; Pomeroy, R. K. Third Chemical Congress of North America, Toronto, 1988, INOR 393. (c) Beringhelli, T.; D'Alphonso, G.; Molinari, H. *Magn. Reson. Chem.* **1986**, *24*, 175.

[13] Keister, J. B.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3304.

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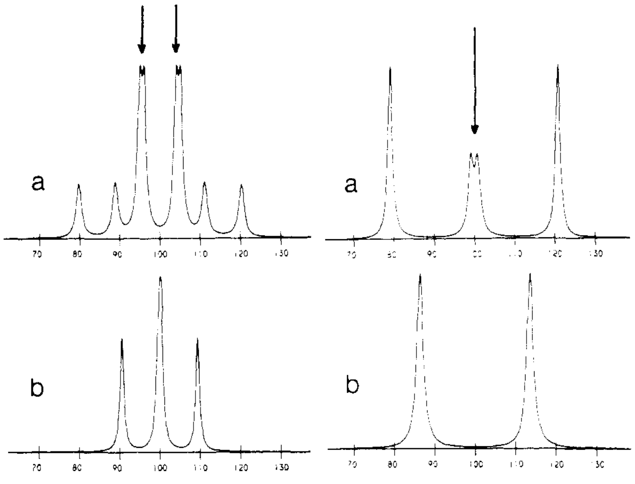
[15] The signal at δ −11.42 due to H2 broadens considerably on cooling, which is attributed to scalar coupling to the ^{14}N nucleus in the trans isocyanide ligand. Severe line narrowing is necessary to distinguish the ^{187}Os satellites at the lower temperatures.



Pt(μ-H)Os Os(μ-H)Os

Figure 2. Simulated subspectra (scale in hertz) for the observable ^{187}Os isotopomers of complex 3, showing the expected satellite patterns for the Os(μ-H)Os resonance and the Os(μ-H)Pt resonance at (a) the slow-exchange limit, and (b) the fast-exchange limit. Arrows indicate the positions of the intense central resonances.

238 K for both resonances are thus clearly compatible with *static* hydrides.

Throughout the temperature range $J(^{195}Pt-H2)$ and $J(^{31}P-H2)$ remain constant, implying that H1 visits all Os–Os edges, and H2 visits all Os–Pt edges, *with retention of the stereochemical integrity* of the Pt(H)(PCy$_3$)(CNCy) [PtL$_3$] unit. This may occur in either a degenerate fashion by rotation of the PtL$_3$ unit about the pseudo 3-fold axis coupled with conrotary motion of H1 to an adjacent Os–Os edge (Scheme I) or a similar nondegenerate two-step process involving an isomer 3′. Since no other hydride signals are observed at any temperature, the former option is more plausible. This mechanism is tantamount to the mutual exchange of the three observable ^{187}Os isotopomers and implies that all Os atoms become chemically equivalent. It also requires effective inter-Os carbonyl exchange, which is indeed observed (see below). The proposed transition-state geometry has the PtL$_3$ unit rotated by 60°, such that the hydride is μ_3 and the phosphine ligand lies over a PtOs$_2$ face. This is exactly the ground-state geometry observed[17] for the PtL$_3$ unit in the cluster Fe$_3$Pt(μ_3-H)(μ_3-COMe)(CO)$_{10}$(PPh$_3$). Due to the threefold degeneracy, a μ_3 orientation for H1 is also intuitively attractive, and EHMO calculations carried out on this model suggest that this is not energetically unlikely.[18]

According to the proposed mechanism (Scheme I) the observed *averaged* ^{187}Os couplings (at 298 K) are given (in terms of the *static* couplings) by $^1/_3\{2(^1J(Os2/3-H1) + {}^2J(Os1-H1)\}$ and $^1/_3\{2(^2J(Os2/3-H2) + {}^1J(Os1-H2)\}$ for H1 and H2, respectively. Estimated values for the (unobservable) *static* two-bond couplings $^2J(Os1-H1)$ and $^2J(Os2/3-H2)$ are 1.7 and 1.2 Hz, respectively (with ^2J values of opposite sign to ^1J). These estimated $^2J(^{187}Os-H)$ magnitudes compare well with that measured directly (1.0 Hz) for Os$_3$(μ-H)$_2$(CO)$_{10}$.[16c] With use of these coupling constants, the mutual exchange of the observable ^{187}Os isotopomers (i), (i′), and (ii) may be simulated and is shown in Figure 2 at the slow- and fast-exchange limits.

Table II. Observed ^{187}Os-H Couplings and Derived Rate and $\Delta G^\ddagger$ Data

temp/K	obsd J(Os–H)[a]	exchange rate[b]/s^{-1}	$\Delta G^{\ddagger b}$/kJ mol^{-1}
238	41.8		
248	41.3	8 (2)	56.1 (7)
252	39.6	17 (1)	55.4 (5)
255	38.6	21 (1)	55.7 (5)
259	37.8	23.5 (5)	56.3 (5)
263	broad		
298	27.3		

[a] Errors in coupling constants ±0.2 Hz. [b] Estimated errors in parentheses.

As the exchange rate increases, the separation of the H1 outer satellite lines initially decreases and the lines then broaden and collapse and then reappear at the smaller separation. For exchange rates between ca. 5 and 50 s^{-1}, this outer line separation is rate sensitive and may be used to derive $\Delta G^\ddagger$ values. Between 248 and 259 K the outer lines are narrow enough for accurate measurement, and observed and derived data are given in Table II. A *mean* value of $\Delta G^\ddagger$ for the exchange of the ^{187}Os isotopomers is estimated at 56 (±1) kJ mol^{-1}. The broadness of the ^{187}Os satellites of H2 at low temperatures precluded comparative measurements for this hydride.

A value for $J_{av}(^{187}Os-H)$ of 18.5 Hz was observed[8] for the hydrides at the fast-exchange limit in complex 1. The mean value of $J_{av}(^{187}Os-H)$ for H1 and H2 [(27.3 + 9.7)/2 = 18.5 Hz], which is the expected *average* ^{187}Os coupling for 3 if the hydrides were undergoing fast mutual exchange, is identical. This suggests, as might be expected, that the ^{187}Os–hydride couplings in 1 and 3 are very similar. The averaging of ^{187}Os couplings to the individual hydrides in 1 cannot be observed because of broadening due to mutual hydride exchange. However, the closely similar CO exchange behavior in 1 and 3 suggests that a common mechanism (i.e. PtL$_3$ rotation) is responsible for the complete scrambling of Os-bound CO's in both clusters. Moreover, the magnitude of $^1J(Pt-C) = 1468$ Hz for the ligating isocyanide carbon observed at ambient temperature also implies that there is no CNCy exchange between Pt and Os centers in 3, mirroring the nonfluxionality of the Pt–CO in 1.[8] From the data obtained for 3, it now seems likely, however, that the H–H exchange and the PtL$_3$ rotation in 1 are not linked processes as was originally suggested[8] but occur as separate fluxional processes (albeit with similar magnitudes of $\Delta G^\ddagger$).

Carbonyl Fluxionality in 3. The variable-temperature $^{13}C\{^1H\}$ NMR spectrum of 3 is shown in Figure 3. Assignments in Table I are based on intensities and couplings[19] to the hydrides. The only ambiguity is the relative assignments of carbonyls b and d, which are both cis to H1. Assignments for these carbonyls are based on the ^{31}P and ^{195}Pt couplings, which are very similar to those observed[8] for the corresponding carbonyls in complex 2, for which assignments are more secure. The fluxional behavior

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(16) For $^1J(^{187}Os-H)$ couplings in Os(μ-H)Os hydrides see: (a) Constable, E. C.; Johnson, B. F. G.; Lewis, J.; Pain, G. N.; Taylor, M. J. *J. Chem. Soc., Chem. Commun.* **1982**, 754. (b) Holmgren, J. S.; Shapley, J. R.; Belmonte, P. A. *J. Organomet. Chem.* **1985**, *284*, C5. (c) Koridze, A. A.; Kizas, O. A.; Kolobova, N. E.; Petrovskii, P. V.; Fedin, E. I. *J. Organomet. Chem.* **1984**, *265*, C33. (d) Colbran, S. B.; Johnson, B. F. G.; Lohoz, F. J.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1988**, 1199. ^{187}Os–H couplings have also been reported for some interstitial hydrides, see: (e) Drake, S. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1988**, 1517.

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(18) Another possibility for the transition state is a butterfly metal geometry resulting from slippage of the PtL$_3$ unit across the Os$_3$ triangle; see ref 7.

(19) It is assumed that trans $^2J(H-C)$ couplings are larger than the corresponding cis couplings. The cis couplings are often small and are barely resolved, though they can usually be detected by increased line widths.

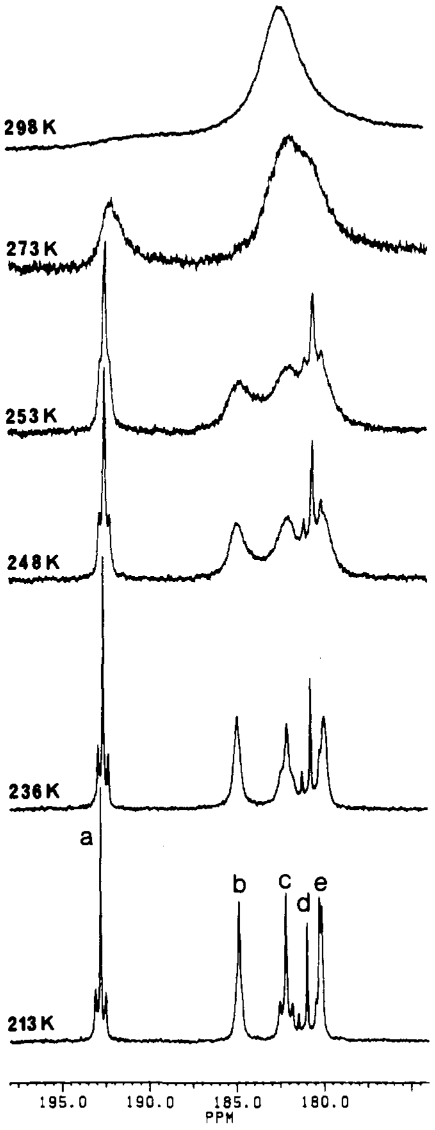

Figure 3. The variable-temperature $^{13}C\{^1H\}$ NMR spectrum of complex 3.

of 3 closely resembles that of 1,[8] with a low-energy tripodal rotation of the two equivalent $Os(CO)_3$ groups b, c, and e causing broadening of these resonances initially, followed by a higher energy process which eventually scrambles all CO ligands. The CO exchange is clearly compatible with the proposed hydride mobility, as all CO's become equivalent at 298 K.

The 2D EXSY NMR experiment[20,21] is a powerful tool for the examination of multisite exchange, and several studies on cluster carbonyl exchange using ^{13}C 2D EXSY have been previously reported.[8,22-25] Quantitative information on individual exchange rates may be obtained from EXSY spectra by either iterative[22,23] or noniterative procedures,[26,27] and these methods have been compared in a recent study.[24] The latter method, discussed in some detail by Abel et al.,[26] assumes negligible off-diagonal elements for the relaxation matrix **R**, i.e. all cross relaxation rates (σ_{ij}'s) are zero. It allows all individual exchange rate constants to be calculated from the volume intensities of diagonal peaks and cross-peaks of a single EXSY spectrum, without recourse to T_1 measurements and hence is relatively efficient with spectrometer time.

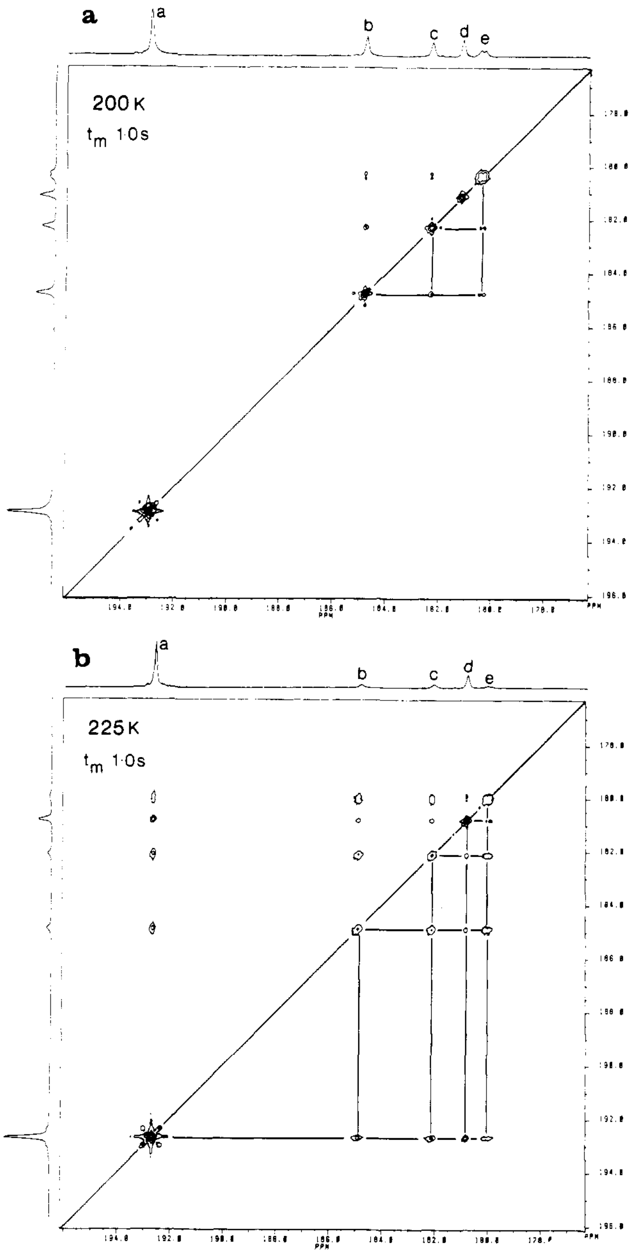

Figure 4. The 2D EXSY $^{13}C\{^1H\}$ NMR spectra of complex 3 at 200 and 225 K.

In addition to the incoherent cross-peak correlations arising between spins involved in chemical exchange, 2D EXSY spectra may also show (a) coherent J cross-peaks[28] between spins which are scalar-coupled (COSY type peaks) and (b) cross-peaks between spins which share a dipolar coupling (NOESY). With the ^{13}C enrichment levels used in this study (ca. 10–20%), the proportion of molecules containing two ^{13}C nuclei is low, and hence both scalar

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[22] Hawkes, G. E.; Lian, L. Y.; Randall, E. W.; Sales, K. D.; Aime, S. *J. Chem. Soc., Dalton Trans* **1985**, 225.

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[25] Lindsell, W. E.; Walker, N. M.; Boyd, A. S. F. *J. Chem. Soc., Dalton Trans.* **1988**, 675.

[26] Abel, E. W.; Coston, T. P. J.; Orrell, K. G.; Sik, V.; Stephenson, D. *J. Magn. Reson.* **1986**, *70*, 34.

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[28] Macura, S.; Huang, Y.; Suter, D.; Ernst, R. R. *J. Magn. Reson.* **1981**, *43*, 259.

Table III. Rate Constants (s^{-1}) from EXSY Spectrum of 3 at 225 K

	k_{ij}[a,b]				
	a	b	c	d	e
a	...	0.14 (7)	0.11 (7)	0.06 (3)	0.12 (7)
b		...	0.89 (28)	0.02 (6)	1.04 (33)
c			...	0.04 (6)	0.73 (24)
d				...	0.09 (12)

[a] $k_{ij} = {}^1/_2 k_{ji}$ for j = d due to population difference. [b] Estimated error in parentheses.

Table IV. NMR Parameters for $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_9(PCy_3)(CNCy)$ (4)

	chem shift[b]/		J[a]/Hz					
reson	ppm	mult[c]	Pt	P	H1	H2	H3a	H3b
			^{13}C Data[d]					
a	184.2	s	66					
b	184.2	d	~4	9.0				2.0
c	181.3	d	70	1.0	2.8		w	
d	180.5	d	26	10.5	w			w
e	180.3	d	56	0.9	2.9	8.0		
f	176.0	s	45		4.3	3.7		
g	175.8	d	25	1.0				
h	174.4	s	5		10.4	3.1		
i	169.9	d	4	1.9	11.5		w	
μ-CH_2	58.6	s						
			^{1}H Data[d]					
H3a	6.95	ddd		1.9	2.7			5.9
H3b	6.57	dd			2.4		5.9	
H2	−15.84	d	533	7.6				
H1	−21.68	ddd	18	1.9			2.7	2.4

[a] w refers to small unresolved coupling. [b] Chemical shifts relative to TMS. [c] Multiplicities for ^{13}C refer to ^{1}H-decoupled spectra. [d] CD_2Cl_2, 298 K.

$J(^{13}C-^{13}C)$ contributions[29] and NOESY contributions are expected to be insignificant. Moreover a recent study on $Os_3(\mu\text{-}H)_2(CO)_{10}$ has shown[30] that $^{13}C-^{13}C$ σ_{ij}'s are negligible even with high ^{13}CO enrichment levels. The cross-peaks observed in this study are thus solely due to chemical exchange, a view confirmed by the observed temperature dependence of the EXSY spectra.

Figure 4 shows the 2D EXSY $^{13}C\{^1H\}$ spectrum for **3** at 200 and 225 K, with a mixing time (t_m) of 1.0 s. At 200 K cross-peaks corresponding to the tripodal rotation of carbonyls b, c, and e are observed, while at 225 K cross-peaks between all signals are seen, confirming complete CO scrambling. With use of the method of Abel et al.[26] individual rate constants were calculated. At 200 K a mean rate of tripodal rotation of 0.17 (±0.03) s^{-1} was estimated, giving $\Delta G^{\ddagger}_{200}$ = 51.7 (±1.0) kJ mol^{-1}. At 213 K a mean rate of 0.75 (±0.3) s^{-1} and a value of 52.1 (±1.2) kJ mol^{-1} for $\Delta G^{\ddagger}_{213}$ were estimated for the same process. These results are comparable with the value of $\Delta G^{\ddagger}_{233}$ = 49.7 (±0.5) kJ mol^{-1} for the analogous process in complex **1**, which was measured by band-shape analysis.[8]

Table III shows the individual rate constants calculated from the EXSY spectrum at 225 K. The rate constants k_{ab} (i.e. the rate of magnetization transfer *from* site a *to* site b), k_{ac}, and k_{de} are all equivalent within error, mean 0.11 (±0.07) s^{-1}, and are also essentially identical with k_{da} = 0.12 s^{-1}. These data are consistent with a rotation of the Pt(H)(PCy_3)(CNCy) group occurring at a rate of 0.11 (±0.07) s^{-1}, giving $\Delta G^{\ddagger}_{225}$ = 58.7 (±1.3) kJ mol^{-1}. The exchange between carbonyls a and d presumably results from the same process, perhaps by a dynamic gearing[31] of the PtL_3 and Os1$(CO)_3$ rotations. There is no evidence for an independent tripodal rotation of Os1$(CO)_3$ occurring before onset of the PtL_3 rotation. The $\Delta G^{\ddagger}$ value calculated for the CO exchange arising from PtL_3 rotation is in reasonable agreement with that calculated for the isotopomer exchange observed in the ^{1}H spectra, and provides good evidence that a single process is responsible for both exchange phenomena.

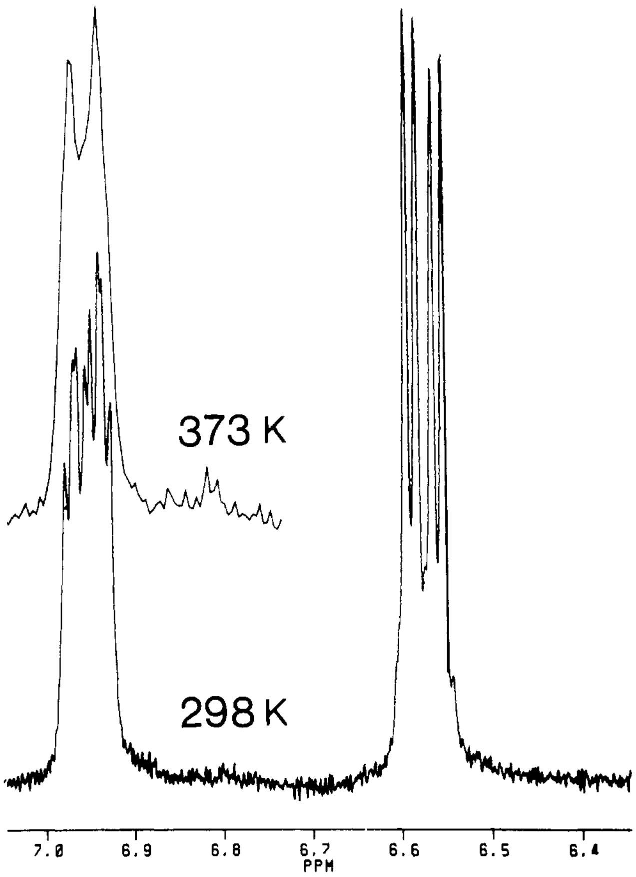

Figure 5. The ^{1}H NMR spectrum of complex **4** in the methylene region. The higher field multiplet is obscured by solvent resonances at 373 K.

Fluxionality in $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_9(PCy_3)(CNCy)$ (4). The two sharp resonances in the ^{1}H NMR spectrum (298 K) of **4** at δ −15.84 and −21.68 are readily assigned, on the basis of ^{195}Pt couplings (Table IV), to the Os(μ-H)Pt and Os(μ-H)Os protons H2 and H1, respectively. Magnetization transfer studies show a slow hydride exchange at this temperature, and from band-shape analysis below the onset of decomposition (ca. 383 K) a value for $\Delta G^{\ddagger}_{373}$ of 85.6 (±0.8) kJ mol^{-1} is estimated for this process. No ^{187}Os couplings could be resolved for either hydride. The chemically distinct endo- and exo-methylene protons H3a and H3b give rise to multiplets (Figure 5) at δ 6.95 and 6.57, respectively. Assignments were based on NOE experiments. Thus saturation of the Os(μ-H)Os hydride (δ −21.68) results in a 3.5% intensity enhancement of the signal at δ 6.95 and an intensity decrease of −0.75% in the signal at δ 6.57. This behavior is characteristic[32] of the indirect NOE's in "linear" ABC

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(29) In addition, the variation applied to t_m reduces J cross peaks; see ref 21b.

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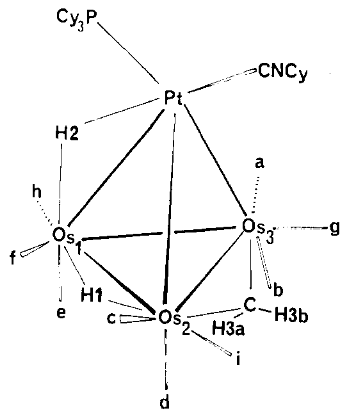


4

systems with short BC distances. The geminal H–H coupling constant of 5.9 Hz is typical[33] of CH_2 groups bridging metal–metal bonds.

In view of previous work showing scrambling between M(μ-H)M hydrides and CH bonds in methylidyne[34,35] and μ-methylene[36] clusters and tautomerizations involving M(μ-H)M and M(μ-H)C intermediates,[37] evidence was sought for similar processes in 4. However, even at 373 K, magnetization transfer experiments showed no detectable exchange between the hydrides and the CH_2 protons. In addition, no evidence for mutual exchange between the methylene protons in 4 was obtained, which contrasts with the fluxional behavior observed for $Os_3(\mu\text{-}CH_2)(CO)_{11}$[38] and $Ru_3(\mu\text{-}CH_2)(CO)_{11}$.[39] The complex multiplet due to H3a collapses at higher temperatures to a simple doublet (J(H–H) = 6.0 Hz, Figure 5). The two methylene protons thus remain chemically distinct and coupled to each other, but coupling to the hydrides and phosphine is being averaged, presumably due to other fluxional processes.

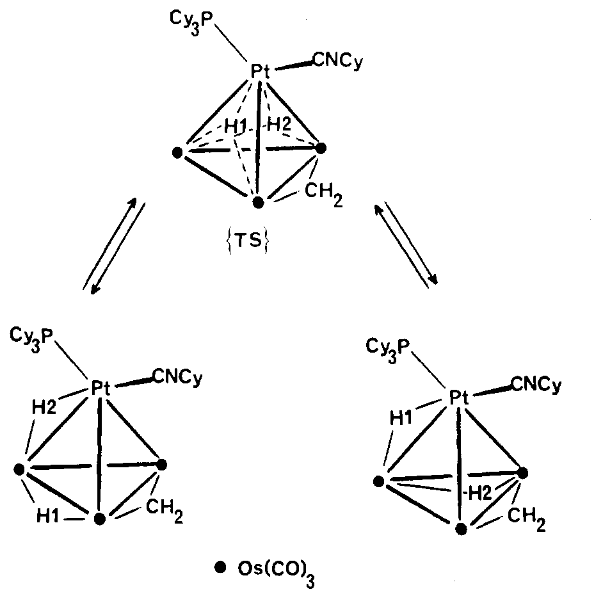
At 298 K the ^{13}C spectrum of 4 shows nine resonances in the CO region (Table IV), in line with the low symmetry of the cluster. All signals are narrow, indicating that carbonyl exchange is slow at this temperature. Resonances e, f, and h may be unambiguously assigned on the basis of hydride couplings; thus resonance e shows a 8.0-Hz coupling to H2 and a 2.9-Hz coupling to H1 and is thus assigned to the carbonyl which is trans to H2 and cis to H1, and similar arguments apply to f and h. Resonance i with a 11.5 Hz coupling to H1 may therefore be assigned to the other CO which is trans to H1. Resonances c and d show small couplings to H1 and are thus assigned to the remaining CO's on Os2, while a, b, and g show no couplings to either hydride and may be assigned to the CO's on Os3. Individual assignments for these latter resonances are based on their ^{195}Pt couplings and on the fluxional behavior observed (see below). The crystal structure of 4 shows[10] that the two CO's in the PtOs2Os3 plane interact weakly with the Pt atom, and hence the resonances a and c, with the largest ^{195}Pt couplings, are assigned to these two CO's. Since resonance i exchanges only with g, a only with c, and d only with b, their assignments follow as shown. Individual assignments of c and d (and hence a and b) may be reversed without affecting arguments about the fluxional behavior.

Table V. Rate Constants (s^{-1})[a] from EXSY Spectrum of 4 at 318 K

$k_{ac,ca}$	0.07 (2)	$k_{bd,db}$	0.09 (2)	$k_{ig,gi}$	0.07 (2)
$k_{ef,fe}$	0.38 (7)	$k_{eh,he}$	0.43 (8)	$k_{fh,hf}$	0.68 (9)
$k_{ag,ga}$	0.02 (1)	$k_{bg,gb}$	0.02 (1)[b]		

[a] Estimated error in parentheses. [b] $k_{ab,ba}$ not measurable due to overlap.

Scheme II



2D EXSY $^{13}C\{^1H\}$ spectra of 4 (shown at 298 and 318 K in Figure 6) demonstrate that slow-exchange processes are occurring. At 298 K cross-peaks are observed between resonances e, f, and h, indicating a tripodal rotation of the $Os1(CO)_3$ group. At 318 K these cross peaks are more intense, and further exchange processes are also evident. Although the pairs of resonances a and b, d and e, and f and g unfortunately become nearly isochronous at this temperature, it is still possible to discern the exchanges occurring. Thus the slope of the *doublet* cross-peak (Figure 6b) unambiguously shows that the *doublet* resonance b exchanges with the *doublet* resonance d (and incidently also shows that the sign of ^3J(P–C) is the same for both resonances[40]). Resonance a exchanges with c and resonance i with either f or g. These pairwise exchanges indicate that the cluster is acquiring a time-averaged mirror plane and hence racemizing. Resonance i must thus be exchanging with g, while the expected exchange between f and h is obscured by the lower energy tripodal rotation which also exchanges these sites. Finally a third exchange process is observed between sites a, b and either g or f, and this is attributed to a tripodal rotation of the $Os3(CO)_3$ group, i.e. resonances a,b exchange with g.

The EXSY spectrum at 318 K was analyzed by the method of Abel et al.,[26] and the results are shown in Table V. Since one diagonal component of each of the doublet resonances b and d is resolved, their total diagonal intensities may reasonably be estimated. Due to overlap,

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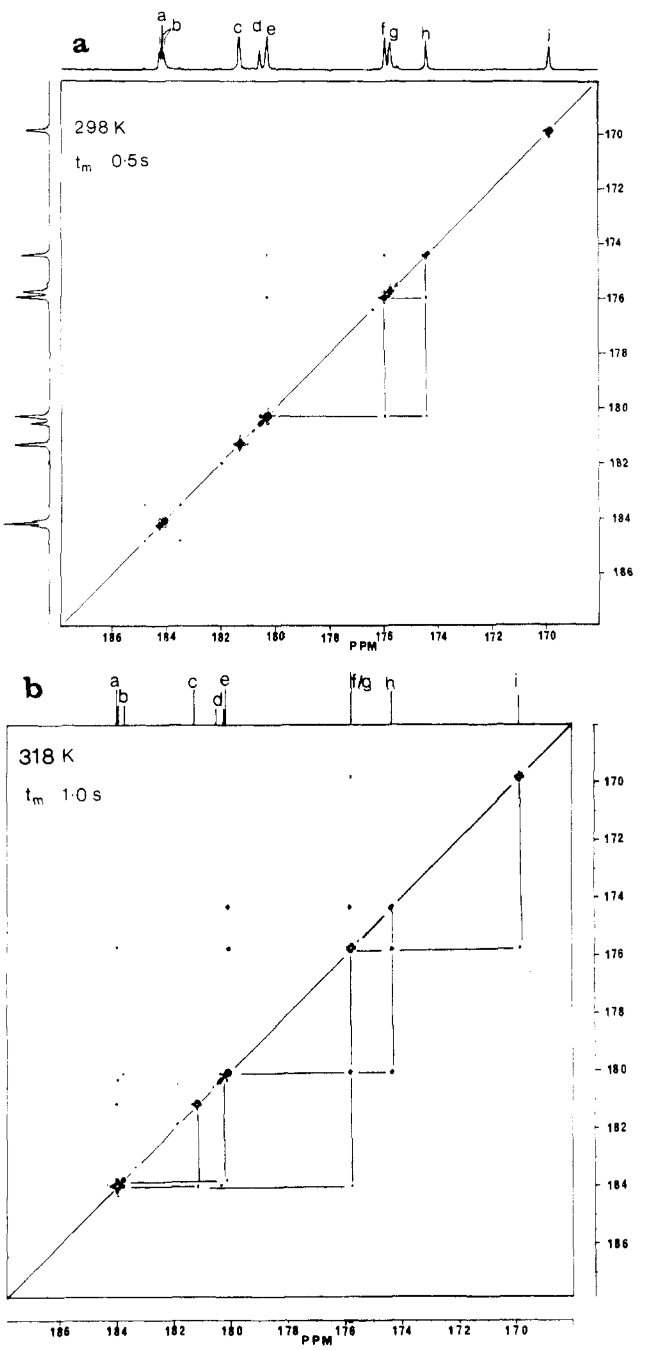

Figure 6. The 2D EXSY $^{13}C\{^1H\}$ NMR spectra of complex 4 at 298 and 318 K.

only the total diagonal intensity for resonances f and g could be measured, and resonance f was (arbitarily) assigned the same diagonal intensity as h. Estimates for the $\Delta G^{\ddagger}_{318}$ values for the three exchange process are 80.5 (±1.0) kJ mol^{-1} for the e/f/g tripodal rotation; 84.7 (±1.1) kJ mol^{-1} for the a/c, b/d, and i/g racemization process; and 88.4 (±1.6) kJ mol^{-1} for the a/b/g tripodal rotation. The $\Delta G^{\ddagger}$ value for the racemization process is the same within error as that estimated for the hydride exchange and suggests that a single process may be responsible. The proposed mechanism is shown in Scheme II. Cluster enantiomerization, by migration of either hydrides[3d,5c,8,41] or other ligands,[3f,42] is a commonly observed process.

The signal at δ 58.6 in the ^{13}C NMR spectrum, shown to be due to a CH_2 carbon by a DEPT experiment, is assigned to the μ-CH_2 group. This chemical shift is outside the Herrmann[33] range (δ 100–210) for μ-CR_2 groups bridging M–M bonds but is similar to the lower values reported for $Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}$ (δ 25.8[36a]), $Os_3(\mu\text{-}CH_2)(CO)_{11}$ (δ 62.5[43]), and $Os_3Pt(\mu\text{-}CH_2)(CO)_{11}(PPh_3)_2$ (δ 76.5[38]).

Conclusions

Dynamic ^{187}Os–hydride couplings allow observation of the effective rotation of the Pt(H)(PCy$_3$)(CNCy) unit in complex 3, which has an estimated $\Delta G^{\ddagger}$ of 56 (±1) kJ mol^{-1}. A similar process has been reported[44] for the Pt(H)L$_2$ unit in several Rh$_2$Pt clusters, and $\Delta G^{\ddagger}$ values are comparable (49.3–58.1 kJ mol^{-1}). The $\Delta G^{\ddagger}$ value for the PtL$_3$ rotation is substantially higher than the predicted[7] barrier for PtL$_2$ rotation. This could be due either (i) to the presence of the Pt–hydride which may stabilize the ground state via Pt(μ-H)Os interactions or (ii) to the coupling of the PtL$_3$ rotation with the migration of the Os(μ-H)Os hydride around the Os–Os edges. In the cluster $[\{Pt(CO)_2\}Pt_3(\mu_3\text{-}CO)(\eta\text{-}C_5Me_5)_3]^+$ the barrier to rotation of the Pt(CO)$_2$ unit about the pseudo 3-fold axis is apparently much lower,[45] and no other migrations are involved. There is no unambiguous evidence for a PtL$_3$ rotation in complex 4, although it should be noted that, without a coupled motion of the Os(μ-H)Os and μ-CH$_2$ groups, such a process would be nondegenerate. Unless the other rotomers had appreciable populations, this process would not be detectable through averaging of CO resonances, since rapid PtL$_3$ rotation does not introduce a new time-averaged symmetry element to a single basal configuration.

2D ^{13}C EXSY is an extremely effective method for mapping the CO exchange network in these clusters, and despite limitations of accuracy due to overlapping signals and relatively low signal-to-noise ratios, quantitative analysis provides useful information about the fluxional processes.

Experimental Section

Complexes 3 and 4 were prepared as previously described,[10] and a sample of 3 was enriched to ca. 10–20% ^{13}C by stirring a dichloromethane solution under an atmosphere of ^{13}CO (99% ^{13}C) for 0.5 h and then refluxing for ca. 1 h to decarbonylate the resulting decacarbonyl adduct. An ^{13}CO-enriched sample of 4 was prepared from previously enriched 3 by treatment with CH_2N_2. ^1H and ^{13}C NMR spectra were obtained on a Bruker WP200 or AM200 FT spectrometer, both equiped with ASPECT 3000 computers, the latter with a process controller and FT array processor. Line-shape analysis was carried out by using a locally

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adapted version of DNMR3.[46] NMR probe temperatures were calibrated by using the method of van Geet[47] and are considered accurate to ±2 K.

$^{13}C\{^1H\}$ EXSY spectra were obtained with either broad-band or composite-pulse ^1H decoupling, using the Bruker automation microprogram NOESY ($D1-\pi/2-D0-\pi/2-D9-\pi/2$–FID–acquire). The data table was acquired by using 1024 words in the F_2 dimension and 256 words in the F_1 dimension zero-filled to 512. Spectral widths were typically 1 kHz, and recycle delays ($D1$) typically 4–6 s. The initial value of the incremented delay $D0$ was 3 μs. For the low-temperature experiments, a cycle of either 8 or 16 scans were acquired for each F_2 FID, with total acquisition times of ca. 4–8 h. A random variation of ±15% was applied to the mixing time delay t_m ($D9$) to reduce any correlations arising from scalar coupling. Apodization was applied to all data sets before Fourier transform, using either $\pi/6$ shifted sine-bell or exponential line-broadening (LB = 2) functions. EXSY spectra were symmetrized about the $F_1 = F_2$ diagonal. For complex **4** the volume integrals, corresponding to the diagonal and off-diagonal elements of the intensity matrix, were obtained by integration of the submatrix rows of the EXSY spectra containing the most intense peaks (usually six to ten rows). For complex **3** integrations were carried out both in the above manner and also by using the box-integral routine of the Bruker AP2D display program. Errors in the integrals were estimated from the integrated intensity of identical sized boxes in noise areas of the EXSY spectrum. There was satisfactory agreement between the derived rate data using either method. Individual exchange rate constants were obtained from the intensity matrix by using the program D2DNMR.[26]

Due to the possibility that apodization functions could adversely affect relative line widths, and hence relative intensities, the effect of using (a) no apodization, (b) $\pi/6$ shifted sine-bell, and (c) Lorentz–Gaussian line narrowing on the data for **3** at 225 K was examined. Apart from the rates associated with the b/c/e tripodal rotation, which appear ill-conditioned in this analysis, there were no serious discrepancies. Rates for the exchanges associated with the PtL_3 rotation varied from ca. 0.1 to 0.2 s^{-1}, which are within the range of the reported rate errors. The discrepancies seen for the b/c/e exchange rate constants (which must be regarded as unreliable at 225 K) are attributed to experimental errors arising from the broadness of the diagonal peaks and cross-peaks associated with this process, overlap of some ^{195}Pt satellites, and generally poor S/N ratios. In order to a ensure a reasonably constant temperature over the whole experiment, the low-temperature acquisitions were limited to a ca. 8-h time period, allowing only a maximum of 16 transients per $D0$ increment.

Acknowledgment. Dr. David Stephenson (Exeter) is thanked for a copy of the 2D EXSY kinetic analysis program D2DNMR and Johnson-Matthey for a generous loan of Pt salts.

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Experimental, Structural, and Theoretical Studies of Diplatinum Complexes Containing Bridging Phenylethenylidene Ligands Including the Excited-State Chemistry and Photophysics of Photochemically Generated Species

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The results of a comprehensive investigation of the chemistry of the diplatinum compound $[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_4]BF_4$ (**1**) and related derivatives are presented. Complex **1** reacts with halides, NCS^-, and various RS^- nucleophiles to give the neutral compounds $[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_3X]$ with loss of one PEt_3 ligand. These Pt_2X complexes react with acid and X^- nucleophile to give the neutral compounds $[Pt_2(\mu\text{-}C{=}CHPh)(PEt_3)_3X_2]$ upon loss of phenylacetylene. The X-ray structures of the Pt_2Cl, Pt_2I, and Pt_2Br_2 complexes have been determined. $[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_3Cl]$: monoclinic; $P2_1/c$; $Z = 4$; $a = 11.685$ (1) Å, $b = 20.810$ (7) Å, $c = 19.172$ (4) Å; $\beta = 123.96$ (1)°. $[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_3I]$: orthorhombic; $Pbca$; $Z = 8$; $a = 18.004$ (3) Å, $b = 22.805$ (4) Å, $c = 19.328$ (4) Å. $[Pt_2(\mu\text{-}C{=}CHPh)(PEt_3)_3Br_2]$: monoclinic; Cc; $Z = 8$; $a = 10.359$ (1) Å, $b = 33.054$ (9) Å, $c = 19.855$ (5) Å; $\beta = 93.40$ (2)°. SC–MEH–MO calculations of the electronic structure of compound **1** indicate a large negative charge on each of the Pt atoms which is reminiscent of the results reported earlier from similar calculations on the anion $Pt_2(P_2O_5H_2)_4^{4-}$. Similarities between the photochemistry of the complexes reported herein and that known for $Pt_2(P_2O_5H_2)_4^{4-}$ are presented. Complex **1** reacts with MeI under photolysis to give Pt_2I and Pt_2I_2, and it reacts as a catalyst under photolysis to produce acetone and molecular hydrogen from 2-propanol. The complex Pt_2Cl emits a red-orange luminescence at 696 nm in a 4:1 ethanol/methanol matrix at 77 K upon excitation at 410 nm. This luminescent state has an average lifetime of 1.7 μs and is attained with an "optical" quantum yield of 0.010 (2).

One of us has reported recently that the cationic diplatinum complex $[Pt_2(\mu\text{-}C{=}CHPh)(C{\equiv}CPh)(PEt_3)_4]BF_4$ (**1**), is formed readily by the addition of the Pt—H bond of $[HPt(PEt_3)_2(acetone)]BF_4$ across one of the C≡C triple