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Ligand substitution in $1,2-Os_3(CO)_{10}(MeCN)_2$ by the diphosphine $(PhO)_2PN(Me)N(Me)P(OPh)_2$: X-ray diffraction structure of $1,2-Os_3(CO)_{10}[(PhO)_2PN(Me)N(Me)P(OPh)_2]$ and DFT investigation of the isomeric $Os_3(CO)_{10}[(PhO)_2PN(Me)N(Me)P(OPh)_2]$ clusters

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ABSTRACT

The diphosphine 1,2-bis(diphenoxyphosphino)-1,2-dimethylhydrazine, $(PhO)_2PN(Me)N(Me)P(OPh)_2$, reacts with 1,2-Os₃(CO)₁₀(MeCN)₂ (1) to afford the corresponding ligand-bridged cluster 1,2-Os₃(CO)₁₀[(-PhO)₂PN(Me)N(Me)P(OPh)₂] (**2b**) in high yield. The product cluster has been characterized in solution by IR and NMR spectroscopy, and the solid-state structure determined by X-ray crystallography. Cluster **2b** is thermally robust, and shows no evidence for formation of the corresponding chelated isomer 1,1-Os₃(CO)₁₀[(PhO)₂PN(Me)N(Me)P(OPh)₂] (**2c**) in refluxing toluene. The energetics for the bridged and chelated clusters have been evaluated by electronic structure calculations, and the thermodynamic preference for the ligand-bridged isomer has been confirmed. DFT calculations on the known bridged and chelated diphosphine isomers of Os₃(CO)₁₀(dppe) clusters have also been performed, and these data are contrasted with clusters **2b** and **2c**.

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1. Introduction

The reactivity of the labile cluster $1,2-Os_3(CO)_{10}(MeCN)_2$ (1) with a variety of diphosphine ligands (P—P) has been investigated with respect to the coordination mode adopted by the ancillary diphosphine ligand at the cluster polyhedron [1–9]. The well-known diphosphine ligands dppm, dppe, dppp, and dppb, all of which possess a saturated carbon backbone, react with 1 to give $1,2-Os_3(CO)_{10}(P-P)$ as the principal product of ligand substitution (Eq. (1) [1–3,5]). These products are stable with respect to intramolecular isomerization to the corresponding chelated species $1,1-Os_3(CO)_{10}(P-P)$.



Compared with the diphosphine ligands in Eq. (1), the ligands depicted in Scheme 1, all of which are structurally rigid and possess an unsaturated two-carbon backbone, react with cluster 1 to afford $1,2-Os_3(CO)_{10}(P-P)$ as the kinetic product of ligand substitution [10–13]. These diphosphine-bridged isomers are unstable, and they readily transform into the corresponding chelated isomer in a non-dissociative, unimolecular process that is unaffected by the presence of trapping ligands. A recent DFT study has provided compelling evidence for a rate-limiting step that involves the merry-go-round exchange of two equatorial CO groups and one of the phosphine moieties [14]; Eq. (2) illustrates this particular transformation in the case of the ligand 1,2-(Z)-bis(diphenylphosphino)ethylene.



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Scheme 1. Diphosphine ligands that exhibit bridge-to-chelate isomerization in Os₃(CO)₁₀(P-P).

In this report we present our results on the reaction between the bis(phosphanyl)hydrazine ligand 1,2-bis(diphenoxyphosphino)-1,2-dimethylhydrazine and $1,2-Os_3(CO)_{10}(MeCN)_2$ (1). Here the new cluster $1,2-Os_3(CO)_{10}[(PhO)_2PN(Me)N(Me)P(OPh)_2]$ (2b) has been isolated and characterized in solution by a combination of NMR and IR spectroscopies. 2b represents the first structurally characterized polynuclear cluster that has possesses this particular bis(phosphanyl)hydrazine ligand [15]. The bridging of adjacent osmium centers in **2b** by the ancillary diphosphine ligand has been established by X-ray crystallography. Cluster 2b is stable in refluxing toluene, and unlike those diphosphine ligands depicted in Scheme 1, shows no evidence for isomerization to the chelated isomer **2c**. The energy difference between the bridged and chelated isomers of Os₃(CO)₁₀[(PhO)₂PN(Me)N(Me)P(OPh)₂] has been determined by DFT calculations, with the diphosphine-bridged cluster computed to be the thermodynamically more stable isomer.

2. Experimental section

2.1. Materials and instrumentation

The bis(acetonitrile) cluster $1,2-Os_3(CO)_{10}(MeCN)_2$ (1) was synthesized from $Os_3(CO)_{12}$ [16]; the latter cluster was prepared via the high-pressure carbonylation of OsO₄ in EtOH solvent [17]. The diphosphine (PhO)₂PN(Me)N(Me)P(OPh)₂ was prepared from 1,2-bis(dichlorophosphino)-1,2-dimethylhydrazine and phenol [18]. The OsO₄ used in our studies was purchased from Engelhard Chemical Co, while the chemicals Me₃NO₂XH₂O, 1,2-dimethylhydrazine dihydrochloride, PCl₃, and phenol were purchased from Aldrich Chemical Co. The anhydrous Me₃NO employed in our studies was obtained from Me₃NO \cdot xH₂O, after the waters of hydration were azeotropically removed under reflux, using benzene as a solvent. All reaction solvents were distilled from a suitable drying agent under argon or obtained from an Innovative Technology (IT) solvent purification system. When not in use all purified solvents were stored in Schlenk storage vessels equipped with highvacuum Teflon stopcocks [19]. The CDCl₃ NMR solvent was purified by bulb-to-bulb distillation from P₂O₅.

The IR spectrum was recorded on a Nicolet 6700 FT-IR spectrometer in amalgamated NaCl cells having a 0.1 mm path length. The ¹H NMR spectral data were recorded at 400 MHz or 500 MHz on Varian VXR-400 and VXR-500 spectrometers, respectively. The ³¹P NMR spectra were recorded at 202 MHz on the latter spectrometer, and these data were collected in the proton-decoupled mode and referenced to external H₃PO₄ (85%), whose chemical shift was set at δ = 0.

2.2. Synthesis of 1,2-Os₃(CO)₁₀[(PhO)₂PN(Me)N(Me)P(OPh)₂] (2b)

To 0.25 g (0.27 mmol) of cluster **1** in a medium Schlenk tube was added 50 mL of CH₂Cl₂ at room temperature, followed by the dropwise addition of 0.14 g (0.29 mmol) of (PhO)₂PN(Me)N(-Me)P(OPh)₂ in 10 mL of CH₂Cl₂. The solution was stirred overnight, after which time TLC analysis, using a 2/3 mixture of CH₂Cl₂/hexane as the eluent, revealed the presence of a single spot (R_f = 0.64) corresponding to the diphosphine-bridged cluster. The solvent was removed under vacuum, and the resulting residue was purified by column chromatography over silica using a 4:1 mixture of CH₂Cl₂/hexane as the mobile phase. The isolated product was recrystallized from benzene/hexane to afford 0.37 g (93% yield) of 1,2-Os₃(CO)₁₀[(PhO)₂PN(Me)N(Me)P(OPh)₂]. IR (CH₂Cl₂): v(CO) 2086 (m), 2021 (m), 2005 (vs), 1976 (m), 1945 (m) cm⁻¹. ¹H NMR (CDCl₃): δ 2.80 (6H, d, Me, ³*J*_{P-H} = 6.5 Hz), 7.00–7.25 (20H, m, aryl). ³¹P NMR (CDCl₃): δ 106.90 (s).

2.3. X-ray crystallographic data

Single crystals of cluster 2b suitable for X-ray diffraction analysis were grown from a *p*-xylene/hexane solution at room temperature. The diffraction data were collected on a Bruker SMART APEX2 CCD-based X-ray diffractometer at 296(2) K. We were unable to collect a dataset at low temperature (<223 K) due to excessive cracking of the crystal, which in turn led to difficulty in finding suitable parameters for the unit cell. Data collection, indexing, and initial cell refinements were carried out using APEX2 [20], with frame integration and final cell refinements done using SAINT [20]. The molecular structure of 2b was determined using direct methods and Fourier techniques, and the data were refined by full-matrix least-squares. An absorption correction, including a face-indexed absorption correction, was applied using the program SADABS [20]. All non-hydrogen atoms were refined anisotropically. The crystal contained a highly disordered molecule of p-xylene that occupies a special position in the cell, and the solvent was appropriately treated by PLATON/SQUEEZE [21]. This correction of the X-ray data (47 electron/cell) was close to the required value for one C_8H_{10} molecule per the full unit cell (58 electron/cell). All hydrogen atoms in the structure were positioned geometrically and were refined as riding atoms attached to the carbon atom. Structure solution, refinement, graphics and generation of publication materials were performed using the available SHELXTL software [22]. The X-ray data and processing parameters are reported in Table 1, with selected bond distances and angles quoted in Table 2.

Table 1

X-ray crystallographic data and processing parameters for $1,2-Os_3(CO)_{10}[(PhO)_2PN(-Me)N(Me)P(OPh)_2]$ (**2b**).

CCDC entry no.	729793
Cryst system	Triclinic
Space group	P-1
a (Å)	11.6081(4)
b (Å)	14.2034(5)
c (Å)	15.4030(6)
α (°)	75.460(1)
β (°)	74.480(1)
γ (°)	68.036(1)
$V(Å^3)$	2236.7(1)
Mol formula	$C_{36}H_{26}N_2O_{14}Os_3P_2{\cdot}0.5C_8H_{10}$
fw	1396.21
Formula units per cell (Z)	2
D_{calcd} (Mg/m ³)	2.073
λ (ΜοΚα), Å	0.71073
$\mu (\mathrm{mm}^{-1})$	8.637
Absorption correction	Semi-empirical from equivalents
Abs corr factor	0.6575/0.2783
Total reflections	28314
Independent reflections	10002
Data/res/parameters	10002/0/504
$R1^{a} [I \geq 2\sigma(I)]$	0.0270
wR2 ^b (all data)	0.0559
GOF on F^2	1.018
$\Delta ho(\max), \Delta ho(\min) (e/A^3)$	1.411, -0.959

^a $R1 = \sum ||F_0| - |F_c|| / \sum |F_0|.$

^b $R2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}.$

Table 2

Selected bond distances (Å) and angles (°) in 1,2-Os $_3(CO)_{10}[(PhO)_2PN(Me)N(Me)-P(OPh)_2]$ (**2b**).

Bond distances			
Os(1)-Os(2)	2.8899(2)	Os(1)-Os(3)	2.8756(3)
Os(2)-Os(3)	2.9105(3)	Os(1) - P(1)	2.268(1)
Os(2)—P(2)	2.272(1)	P(1) - N(1)	1.674(4)
P(2) - N(2)	1.673(4)	N(1)-N(2)	1.430(5)
N(1)-C(35)	1.490(5)	N(2)-C(36)	1.473(6)
$P(1) \cdots P(2)$	3.573(2)		
Bond angles			
P(1) - Os(1) - Os(3)	154.03(3)	P(1) - Os(1) - Os(2)	93.51(3)
P(2) - Os(2) - Os(3)	163.22(3)	P(2) - Os(2) - Os(1)	103.84(3)
N(1) - P(1) - Os(1)	122.7(1)	N(2) - P(2) - Os(2)	120.1(1)
N(1)-N(2)-P(2)	119.7(3)	N(2) - N(1) - P(1)	114.8(3)
C(36) - N(2) - P(2)	119.7(3)	C(35) - N(1) - P(1)	120.5(3)
N(1)-N(2)-C(36)	110.4(4)	N(2)-N(1)-C(35)	117.3(3)

2.4. Computational methodology and modeling details

The reported calculations were performed with the hybrid DFT functional B3LYP, as implemented by the Gaussian 09 programming package [23]. This functional utilizes the Becke three-parameter exchange functional (B3) [24], combined with the correlation functional of Lee, Yang and Parr (LYP) [25]. The Os atoms were described by Stuttgart–Dresden effective core potentials (ecp) and SDD basis set, while the 6-31G(d') basis set, as implemented in the Gaussian 09 program, was employed for the remaining atoms.

All reported geometries were fully optimized, starting from the X-ray crystallographic structure when available, and evaluated for the correct number of imaginary frequencies through calculation of the vibrational frequencies, using the analytical Hessian. Species with zero imaginary frequencies (positive eigenvalues) correspond to a stationary point or minimum, whereas an imaginary frequency (negative eigenvalue) designates a transition state. The transition state connecting the isomeric clusters Os₃(CO)₁₀[(PhO)₂PN(Me)N(-Me)P(OPh)₂] and Os₃(CO)₁₀(dppe) was also examined by IRC calculations (both directions) to verify the nature of the reactant and product in the merry-go-round process. The computed frequencies were used to make zero-point and thermal corrections to the electronic energies; the reported potential energies and enthalpies are quoted in kcal/mol relative to the specified standard [26]. The geometry-optimized structures have been drawn with the JIMP2 molecular visualization and manipulation program [27].

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

Cluster **1** reacts with $(PhO)_2PN(Me)N(Me)P(OPh)_2$ in CH_2Cl_2 at room temperature to furnish the diphosphine-bridged cluster $1,2-Os_3(CO)_{10}[(PhO)_2PN(Me)N(Me)P(OPh)_2]$ (**2b**), as verified by TLC analysis and spectroscopic monitoring of the reaction solution. **2b** was isolated in 93% yield as the sole observable product by column chromatography over silica gel, followed by recrystallization. While **2b** is relatively stable toward oxygen in the solid state over the course of several days, solutions containing the product exhibited noticeable decomposition over the same period when exposed to oxygen.

2b was characterized in solution by IR, ¹H and ³¹P NMR spectroscopies. The IR spectrum recorded in CH₂Cl₂ exhibits terminal



Fig. 1. Displacement ellipsoid plot of the molecular structure of the non-hydrogen atoms of **2b** at the 30% probability level (left), and the optimized B3LYP structure of **2b** (right). The bond distances specified in the B3LYP structure are reported in angstrom.

carbonyl stretching bands at 2086 (m), 2021 (m), 2005 (vs), 1976 (m), and 1945 (m) cm⁻¹, and these frequencies and their relative intensities are comparable to those data reported for related diphosphine-bridged Os₃ clusters [1–3,7,10–14]. The ¹H NMR spectrum displayed a doublet for the two methyl groups at δ 2.80 and the twenty aryl hydrogens appeared as an overlapping set of resonances from δ 7.00–7.25. The singlet resonance found in the ³¹P{¹H} NMR spectrum at δ 106.90 is consistent with the formulated structure, and this confirms that the reaction between **1** and the bis(phospanyl)hydrazine ligand yields **2b** as an isomerically pure product. Coordination of the bis(phosphanyl)hydrazine ligand to the triosmium core in **2b** leads to a pronounced upfield ³¹P shift relative to the free ligand (δ 138.16) recorded under identical conditions.

3.2. X-ray diffraction structure of 2b

The unequivocal disposition of the bis(phosphanyl)hydrazine ligand relative to the cluster polyhedron in the isolated product was established by X-ray crystallography. Fig. 1 (left-hand side) shows the displacement ellipsoid plot of cluster **2b**, which confirms the coordination of the Os(1) and Os(2) centers by the bis(phosphanyl)hydrazine ligand. The bridging of adjacent osmium centers in **2b** by the bis(phosphanyl)hydrazine auxiliary does not adversely affect the triangular array of osmium atoms, whose three Os-Os vectors, which are more or less identical in length, exhibit a mean distance of 2.892 Å. The mean Os-P bond distance of 2.270 Å is slightly longer than the mean Co–P distance of 2.156 Å reported by us for ligand-bridged cluster PhCCo₃(CO)₇[(MeO)₂PN(Me)N(-Me)P(OMe)₂] [15]. While numerous mononuclear compounds that possess a chelating R₂PNR'NR'PR₂ ligand (where R = alkyl, aryl, alkoxides; R' = Me, Et) have been prepared [28–31], the coordination chemistry of these ligands with polynuclear metal clusters remains largely unexplored. To our knowledge, 2b and PhCCo₃(CO)₇[(-MeO)₂PN(Me)N(Me)P(OMe)₂] represent the only structurally characterized polynuclear clusters containing these ligands, and here the ancillary bis(phosphanyl)hydrazine ligand serves to bind two adjacent metal centers. One factor that has hampered a more thorough investigation of the ligand substitution chemistry of bis(phosphanyl)hydrazine ligands at metal clusters is the facile fragmentation of the diphosphine ligand that occurs upon coordination [32].

The P(1)—N(1) [1.674(4) Å], P(2)—N(2) [1.673(4) Å], and N(1)—N(2) [1.430(5) Å] distances are comparable to those distances in PhCCo₃(CO)₇[(MeO)₂PN(Me)N(Me)P(OMe)₂] [15], W(CO)₄[(PhO)₂PN(Me)N(Me)P(OPh)₂] [28], and CpRuCl[(PhO)₂PN(-Me)N(Me)P(OPh)₂] [29]. The N(1) and N(2) atoms are best viewed as trigonal planar since of the sum of angles about each nitrogen center is 352.6° and 349.8°, respectively. The internuclear P(1)…P(2) distance of 3.573(2) Å in **2b** is comparable to the



Fig. 2. Potential energy surface for the merry-go-round isomerization of **2b** to **2c**. The geometry-optimized structures for species **TS2b2c** and **2c** are included, and the energy values are represented as $\Delta E(\Delta H)$ in kcal/mol with respect to **2b**.

internuclear P···P distance found in the bridged isomer of Os₃(-CO)₁₀(dppq) and Os₃(CO)₁₀(dppbz) [13,14]. The ten carbonyl groups are all linear and exhibit bond distances and angles consistent with their linear nature. The angle subtended by the Os(1)–P(1)–N(1) [122.7(1)°] and Os(2)–P(2)–N(2) [120.1(1)°] linkages is unexceptional relative to other phosphine-bridged Os₃(-CO)₁₀(PP) clusters of this genre. The remaining bond distances and angles are unremarkable and require no comment.

3.3. Thermal isomerization of 2b to 2c and DFT studies

The isomerization of **2b** to the corresponding chelated isomer $1,1-Os_3(CO)_{10}[(PhO)_2PN(Me)N(Me)P(OPh)_2]$ (**2c**) was next explored, as part of our interest in the chemical reactivity of polynuclear cluster compounds [33]. It was anticipated that heating **2b** would furnish **2c** without complications, based on the facile rearrangement of the diphosphine ligand in different $Os_3(CO)_{10}(P-P)$



Scheme 2. Merry-go-round exchange process for the isomeric clusters 2 and 3.

systems already investigated by us. Samples of **2b** were found to be stable in refluxing toluene! The isomerization reaction was not examined at higher temperatures in order to avoid dissociative loss of CO from **2b**, a process that becomes competitive at elevated temperature (>110 °C). This deleterious manifold would afford the unsaturated cluster $Os_3(CO)_9(P-P)$, which has been shown to serve as the bifurcation point for ortho metalation and irreversible degradation of the diphosphine ligand by P–C bond cleavage in related systems [10,34].

To gain a greater understanding on the responsible factor(s) for the unobserved isomerization reaction, the ground-state energies of 2b and 2c and the energetics for the merry-go-round isomerization were investigated by DFT calculations. Scheme 2 illustrates this bridge-to-chelate isomerization process. The B3LYP-optimized structures of **2b** and **2c** were computed. The DFT structure of **2b** is depicted in Fig. 1 alongside the X-ray structure, allowing for a direct comparison. Overall, there is good agreement between the diffraction and DFT structures for the diphosphine-bridged cluster. The DFT structure computed for 2c is shown in Fig. 2, where it is confirmed that 2b lies 6.8 kcal/mol lower in enthalpy than 2c. The absence of **2c** on heating is fully consistent with the experimental data and the DFT computed K_{eq} value of ca. 10^{-3} in refluxing toluene for the $2b \Rightarrow 2c$ transformation. The conversion of 2b to **2c** was found to occur in a one-step process through the triply bridged transition structure TS2b2c. Here the concerted merrygo-round motion of an equatorially disposed phosphine and two CO groups represents the lowest energy pathway for the isomerization [14]. That TS2b2c serves as a transition-state structure and not a high-energy stationary point on the potential energy surface (PES) for the isomerization was verified by normal mode analysis, which revealed an imaginary frequency of 61*i* for TS2b2c. Subsequent IRC calculations confirmed that TS2b2c connects 2b directly to 2c. While the barrier for the isomerization is high, it is the ground-state energy difference between the isomeric clusters that retards the isomerization.

Our previous studies on the ligand isomerization in $Os_3(CO)_{10}(P-P)$ have employed diphosphines that possessed an unsaturated backbone, where the vicinal phosphorus centers were tethered to an etheno- or benzo-based platform. In these particular systems, the chelated isomer of $Os_3(CO)_{10}(P-P)$ has been found to be thermodynamically more stable than the corresponding bridged cluster, a trend that is reversed in the case of the (PhO)₂PN(Me)N(-Me)P(OPh)₂ ligand in **2b**. To our knowledge, only one other documented case exists where the bridged isomer is preferred over the chelated isomer, and this involves the cluster $Os_3(CO)_{10}(dppf)$ [where dppf = 1,1'-bis(diphenylphosphino)ferrocene] [35]. Undoubtedly, the isomer preference in Os₃(CO)₁₀(P-P) is controlled by the nature of ancillary diphosphine, with the bite angle of the ligand, the composition of the backbone that tethers the phosphorus centers, and the substituents on the phosphorus and backbone chain representing the critical variables in play.

In the case of **2b** and **2c**, the isomer preference parallels the potential energy profile for internal rotation displayed by hydrazine. Both molecular mechanics (MM) and *ab initio* calculations have shown the vicinal lone-pair orbital interactions between the nitrogen centers in hydrazine to be the dominant factor in determining conformational stability [36,37]. A plot of the potential energy function versus the LP–N–N–LP dihedral angle (where LP = lone pair) in free hydrazine reveals two distinct maxima at 0° and 180° and a single minimum at 90°. The P–N–N–P dihedral angle in **2b** and **2c** is ca. 85° and 41°, respectively, which allows the hydrazine lone-electron pairs in **2b** to achieve a near orthogonal orientation in concert with the preferred conformation found for hydrazine. The B3LYP/TZVP-computed energy profile for hydrazine internal rotation computed by Maginn and coworkers reveals an energy difference of ca. 5 kcal/mol for the conformations at 41° and 90° [37], and this magnitude is in good agreement with the ground-state energy difference computed for clusters **2b** and **2c**.

3.4. DFT evaluation of the bridged and chelated isomers of Os₃(CO)₁₀(dppe)

Having established the greater stability of the bridged isomer **2b** versus **2c**, we wished to probe the isomer preference in a triosmium cluster possessing a diphosphine ligand with a different saturated backbone of comparable spacer length. The ligands 1,2bis(diphenylphosphino)ethane (dppe) and (PhO)₂PN(Me)N(Me)-P(OPh)₂ are analogous since they both contain a two-atom spacer in the form of an ethano versus a hydrazine-based moiety, respectively. The bridged (3b) and chelated (3c) isomers of Os₃(- $CO_{10}(dppe)$, which have been synthesized and structurally characterized several years ago [3,38], provide the ideal pair of clusters in which to test the generality of bridging versus chelating isomer stability in this genre of clusters. The solid-state structures reveal no unusually short inter- or intramolecular contacts, and the dppe ligand exerts no adverse perturbation on the Os₃(CO)₁₀ moiety in each isomer. Thus, any energy difference between the two isomers may be attributed to effects within ancillary diphosphine ligand, as modulated by the coordination mode adopted the ligand.

The PES for the concerted isomerization reaction and the geometry-optimized structures for **3b**, **3c**, and **TS3b3c** are depicted in Fig. 3. The ground-state energy difference in the two dppe-substituted clusters mirrors the trend found in $Os_3(CO)_{10}[(PhO)_2PN(-Me)N(Me)P(OPh)_2]$, with **3b** thermodynamically more stable and 7.3 kcal/mol lower in enthalpy than its chelated counterpart. While the ground-state energy difference between the isomeric clusters **2** and **3** is comparable, the presence of the dppe ligand destabilizes the merry-go-round exchange process in **TS3b3c** 4.0 kcal/mol relative to **TS2b2c**. The kinetic stability of the isomeric clusters based on $Os_3(CO)_{10}(dppe)$ is consistent with the earlier experimental observations of Deeming and coworkers [2].

The isomer preference in $Os_3(CO)_{10}(dppe)$ has its origin in the Pitzer (torsional) and angle strain associated with the different sized rings that result from dppe coordination to the $Os_3(CO)_{10}$ moiety. Examination of the dppe ligand in the six- and five-



Fig. 3. Potential energy surface for the merry-go-round isomerization of **3b** to **3c**. The geometry-optimized structures for species **3b**, **3c** and corresponding transition state **TS3b3c** are included, and the energy values are represented as $\Delta E(\Delta H)$ in kcal/mol with respect to **3b**.

membered ring that is produced in the bridged and chelated isomers, respectively, reveals a greater number of torsional derivations in the latter isomer. The strain about the H–C–P–C_{aryl} linkages in **3c** is particularly pronounced in the case of the one of the two CH₂PPh₂ units. Such a scenario is akin to that used to account for the stability difference between cyclohexane and cyclopentane rings [39].

Clearly the nature of the diphosphine ligand is important as it relates to the energy difference in the ground-state isomers and the activation barrier for the merry-go-round exchange. A measure of the steric effects within the diphosphine ligand can be seen in reaction dynamics of the the cluster $Os_3(CO)_{10}[(Z)-$ Ph₂PCH=CHPPh₂], where the two phosphine moieties are tethered by an etheno platform. Here the chelated isomer lies 1.7 kcal/mol lower in enthalpy than the bridged isomer, and the barrier height (ΔH^{\neq}) for isomerization is on the order of 26 kcal/mol [10]. Relative to the Os₃ cluster containing the ligand (Z)-Ph₂PCH=CHPPh₂, the presence of two extra hydrogens associated with the ethano bridge of the dppe ligand leads to unfavorable steric interactions in the chelated isomer of $Os_3(CO)_{10}(P-P)$ and the transition structure, which in turn leads to a reduction in the overall exothermicity of the isomerization and increases the barrier height for the concerted merry-go-round exchange of phosphine and CO groups.

4. Conclusions

Ligand substitution in 1,2-Os₃(CO)₁₀(MeCN)₂ in the presence of the bis(phosphanyl)hydrazine ligand (PhO)₂PN(Me)N(Me)P(OPh)₂ furnishes for $1,2-Os_3(CO)_{10}[(PhO)_2PN(Me)N(Me)P(OPh)_2]$. The molecular structure of the product has been determined and the bridging of adjacent osmium atoms by the diphosphine confirmed. This product is stable in refluxing toluene and shows no evidence for isomerization to the chelated cluster. The electronic structures of the bridged and chelated isomers have been evaluated by DFT calculations. The ground-state energies computed for the isomeric $Os_3(CO)_{10}[(PhO)_2PN(Me)N(Me)P(OPh)_2]$ clusters establish the bridged isomer as the thermodynamically more species and corroborate our inability to observe spectroscopically the chelated isomer. Isomer thermodynamics and the barrier height to diphosphine rearrangement in the related cluster Os₃(CO)₁₀(dppe) have been computationally examined, and the results contrasted with etheno-based derivatives Os₃(CO)₁₀[(Z)-Ph₂PCH=CHPPh₂]. The saturated backbone in the bis(phosphanyl)hydrazine and dppe ligands destabilizes the chelated isomer relative to the bridged isomer.

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Appendix A. Supplementary material

CCDC 729793 contains the supplementary crystallographic data for 1,2-Os₃(CO)₁₀[(PhO)₂PN(Me)N(Me)P(OPh)₂]; these data may be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/Cif. Atomic coordinates and energies of the optimized stationary points and transition-state structures are available upon request from the author (MGR). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.molstruc.2011.11.037.

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