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Reactivity of Triosmium and Triruthenium Carbonyls with 2,2′-Diamino-1,1′-binaphthalene. Synthesis of C- and N-Metalated Derivatives

Javier A. Cabeza,[*,†] Iván da Silva,[†] Ignacio del Río,[†] Santiago García-Granda,[‡]
Víctor Riera,[†] and M. Gabriela Sánchez-Vega[†,§]

Departamento de Química Orgánica e Inorgánica, Instituto de Química Organometálica “Enrique Moles”, Universidad de Oviedo-CSIC, E-33071 Oviedo, Spain, and Departamento de Química Física y Analítica, Universidad de Oviedo, E-33071 Oviedo, Spain

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The reaction of $[Os_3(MeCN)_2(CO)_{10}]$ with 2,2′-diamino-1,1′-binaphthalene (H_2binam) affords the coordinatively unsaturated trinuclear derivative $[Os_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-Hbinam-}N,C)(CO)_9]$ (**1**), which contains a C-metalated Hbinam ligand attached to an Os atom through an NH_2 group and to the remaining two Os atoms through the metalated C atom. The unsaturation of **1** is somewhat relieved by a weak interaction of a naphthalene C═C double bond with an Os atom. Curiously, treatment of $[Ru_3(MeCN)_2(CO)_{10}]$ with H_2binam does not give the ruthenium analogue of **1**. The stepwise treatment of $[Ru_3(CO)_{12}]$ with LiHbinam and $[HOEt_2][BF_4]$ leads to $[Ru_3(\mu\text{-H})(\mu\text{-}\eta^1\text{-Hbinam-}N)(CO)_{10}]$ (**2**), in which an N-metalated Hbinam acts as an edge-bridging amido ligand. Complex **2** reacts with bis(diphenylphosphanyl)methane (dppm) to give $[Ru_3(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-binam-}C,N)(\mu\text{-}\eta^2\text{-dppm-}P,P)(CO)_7]$ (**3**). This complex contains a doubly C- and N-metalated binam ligand attached to a Ru atom through the metalated C atom and to the remaining two Ru atoms through the metalated NH fragment. Compounds **1** and **3** are the first examples of C-metalated derivatives of H_2binam.

Introduction

The coordination and organometallic chemistry of the atropisomeric ligands 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthalene (binap) and 1,1′-binaphthalene-2,2′-diol (H_2binol) and some of their organic derivatives has been extensively studied[1−5] because many of their enantiomerically pure metal complexes are catalyst precursors for very efficient asymmetric syntheses.[2] Although most of these complexes are mononuclear, some polynuclear clusters have also been prepared.[3−5]

In contrast with the rich transition metal complex chemistry known for binap and H_2binol, noted above, that of 2,2′-diamino-1,1-binaphthalene (H_2binam) and its organic derivatives has been far less investigated.[6−10] In fact, for H_2binam and its N-unsubstituted derivatives, only mononuclear complexes of ruthenium,[7] nickel,[8] palladium,[8,9] and platinum[8] have been reported. Most transition metal derivatives of H_2binam have also been

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[*] To whom correspondence should be addressed. E-mail: jac@sauron.quimica.uniovi.es. Fax: +34-985103446. Internet: http://www12.uniovi.es/investigacion/jac/.

[†] Departamento de Química Orgánica e Inorgánica.

[‡] Departamento de Química Física y Analítica.

[§] On leave from Departamento de Química, Universidad de Carabobo, Bárbula, Venezuela.

(1) A search at the Cambridge Structural Database has revealed the existence of 69 and 48 X-ray structures of transition-metal complexes containing ligands derived from binap and binol, respectively: CSD version 5.23, CCDC, updated Sept 2002.

(2) For relevant reviews on the use of binap[2a−f] and binol[2f,g] complexes in organic synthesis, see: (a) Noyori, R. *Chem. Soc. Rev.* **1989**, *18*, 187. (b) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. (c) Otsuka, S.; Tani, K. *Synthesis* **1991**, 665. (d) Akutagawa, S. *Appl. Catal., A* **1995**, *128*, 171. (e) Kumobayashi, H. *Recl. Trav. Chim. Pays-Bas* **1996**, *115*, 201. (f) Rosini, C.; Franzini, L.; Raffaelli, A.; Salvadori, P. *Synthesis* **1992**, 503. (g) Shibasaki, M.; Sasai, H. *Top. Stereochem.* **1999**, *22*, 201.

(3) For triosmium clusters derived from binap, see: (a) Deeming, A. J.; Stchedroff, M. *J. Chem. Soc., Dalton Trans.* **1998**, 3819. (b) Prestopino, F.; Persson, R.; Monari, M. *Inorg. Chem. Commun.* **1998**, *1*, 302.

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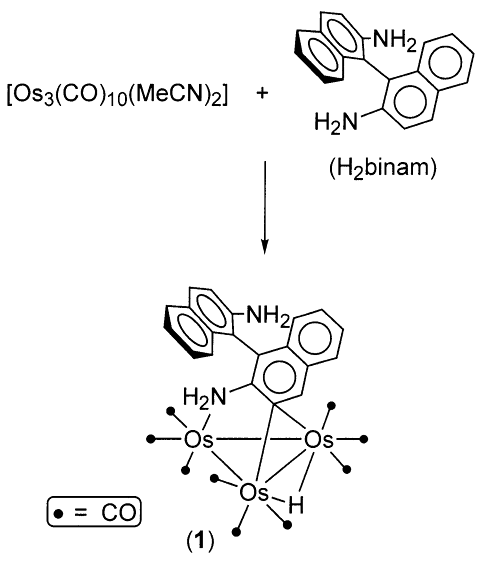
10.1021/om020903w CCC: $25.00

Scheme 1. Synthesis of Compound 1



used as efficient catalyst precursors for asymmetric synthesis.[6−10]

As a continuation of our studies on the reactivity of triruthenium and triosmium carbonyls with amines,[11,12] we decided to study the reactivity of these cluster precursors with H_2binam. We now report not only the synthesis of the first trinuclear complexes derived from H_2binam but also the first examples of complexes in which this ligand is C-metalated.

Results and Discussion

The triosmium acetonitrile complex $[Os_3(MeCN)_2(CO)_{10}]$ reacted with H_2binam, in THF at reflux temperature, leading to the trinuclear derivative $[Os_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-Hbinam-}N,C)(CO)_9]$ (**1**; Scheme 1). No intermediates were detected when the reaction was monitored by IR spectroscopy and spot TLC. No reaction occurred at room temperature.

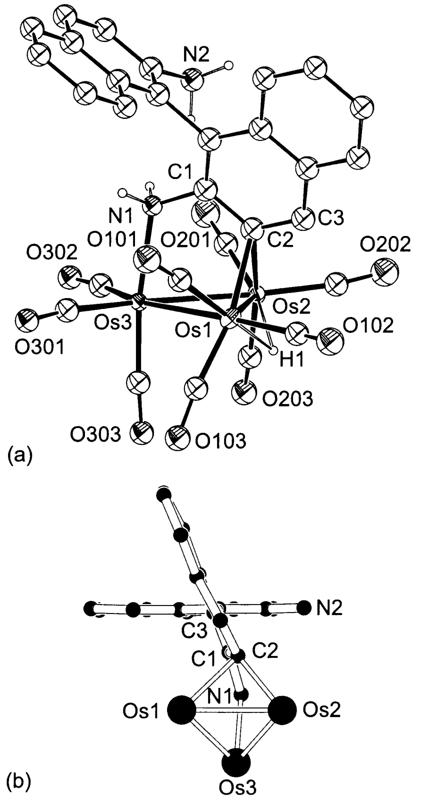


Figure 1. (a) Molecular structure of compound **1** (50% probability level, aromatic H atoms omitted for clarity). (b) View of compound **1** approximately along the planes of the naphthalene rings, showing the disposition of the Hbinam ligand with respect to the metal triangle (carbonyl groups and H atoms omitted for clarity).

Table 1. Selected Interatomic Distances (Å) in Complex 1

Os(1)−Os(2)	2.809(2)	Os(1)−Os(3)	2.850(2)
Os(2)−Os(3)	2.767(2)	Os(1)−C(2)	2.34(3)
Os(1)−C(3)	2.70(3)	Os(2)−C(2)	2.17(3)
Os(2)−C(3)	3.04(3)	Os(3)−N(1)	2.21(2)
C(1)−N(1)	1.45(4)	C(1)−C(2)	1.40(4)
C(2)−C(3)	1.35(4)		

The solid-state structure of complex **1** (Figure 1) was determined by X-ray diffraction on a crystal obtained from a batch made from (*R*)-(+)-H_2binam, since only poor-quality crystals were obtained from racemic H_2binam. A selection of interatomic distances is given in Table 1. The complex consists of a triangle of osmium atoms in which each metal atom is attached to three terminal carbonyl ligands. The metal triangle is capped by a C^3-metalated Hbinam ligand which is attached to an Os atom through an NH_2 group and to the remaining two Os atoms through the metalated C atom. A bridging hydride spans the same edge of the metal triangle as the metalated C atom (Figure 1a). The dihedral angle between the planes of both naphthalene fragments is 66.3(5)°. This ligand arrangement affords an electron count of 46, resulting in a coordinatively unsaturated species. This unsaturation is somewhat relieved by a weak π interaction of the naphthalene C(2)−C(3) double bond with the Os(1) atom that results in the fact that the metal triangle is not perpendicular to the plane of the naphthalene fragment to which it is attached but forms a dihedral angle of 70.0(4)° (Figure 1b). In fact, the Os(2)−C(2) distance, 2.17(3) Å, is shorter than the Os(1)−C(2) distance, 2.34(3) Å, as expected for distances involved in σ and π interactions with a C=C fragment, respectively. The C(2)−C(3) distance, 1.35(4) Å, is typical of an uncoordinated C=C double bond. However, the Os(1)−C(3) distance, 2.70(3) Å, although too long for a normal Os−C bond, reflects some bonding interaction.

In solution, compound **1** was characterized by IR and NMR spectroscopy. Its IR spectrum confirmed the absence of bridging CO ligands. Its ^{1}H and DEPT ^{13}C NMR spectra indicated the C-metalation of a naphthalene fragment, since they show the resonances of 11 CH groups. The chemical shifts of the proton and carbon atoms of these CH groups (8.2−6.8 ppm for ^{1}H and 132−

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[11] For a review on the reactivity of triruthenium carbonyl clusters derived from 2-aminopyridines, see: Cabeza, J. A. *Eur. J. Inorg. Chem.* **2002**, 1559.

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118 ppm for ^{13}C) are within the ranges expected for uncoordinated CH groups of aromatic ligands. Thus, they provide no evidence for the coordination of a naphthalene C=C double bond to osmium. The ^{1}H NMR spectrum also shows the resonances of a hydride (−14.95 ppm) and two distinct NH_2 groups, one with diastereotopic protons (6.10 and 5.12 ppm, doublets, $J = 11.5$ Hz), corresponding to that coordinated to osmium, and other with equivalent protons (3.89 ppm, singlet), which is assigned to the uncoordinated NH_2 group.

The reactions of compound **1** with carbon monoxide and triphenylphosphane were studied. If the compound is indeed unsaturated, then these reactions were expected to take place under mild conditions. Both reactions occurred readily within a few minutes, taking place at room temperature (bubbling CO) or upon mild heating (THF reflux, PPh_3); unfortunately, both gave mixtures of several products that were not characterized.

The C-metalation of aromatic primary and secondary amines, $ArNH_2$ and ArNHR, has been previously observed in very few bi-[13] and trinuclear complexes,[12c,14,15] including the triosmium derivatives $[Os_3(\mu\text{-H})(\mu_3\text{-}\eta^3\text{-Hdan-}C,C,N)(CO)_9]$ (H_2dan = 1,8-diaminonaphthalene),[12c] $[Os_3(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-pfa-}C,N)(CO)_9]$ (H_2pfa = 4-fluoroaniline),[14] $[Os_3(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-ind-}C,N)(CO)_9]$ (H_2ind = indoline),[15] and $[Os_3(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-thquin-}C,N)(CO)_9]$ (H_2-thquin = tetradihydroquinoline),[15] which are coordinatively saturated 48-electron species.

Rosenberg's group has prepared a family of unsaturated 46-electron triosmium complexes, somewhat related to compound **1**, derived from benzoheterocycles containing pyridinic nitrogens, corresponding to the formulation $[Os_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-L-}N,C)(CO)_9]$ (HL = quinoline, 5,6-benzoquinoline, quinoxaline, 2-methylbenzotriazole, 2-R-benzothiazole, 2-R-benzimidazole, 2-R-benzoxazole, and some C-substituted or partially hydrogenated derivatives).[16] The μ_3-η^2-N-heterocyclic ligands of all these compounds are perpendicular to the trimetallic plane, interacting with an Os atom through the N atom (2-electron donor) while spanning an Os−Os edge through the *C*-metalated benzo group (1-electron donor). When treated with amines and phosphanes, these unsaturated compounds are generally transformed into electron-precise derivatives containing μ-η^2-heterocyclic ligands.[16a,17] Interestingly, electron-precise derivatives containing a σ,π-vinyl interaction (3-electron donor), in addition to the N coordination, are formed when the unsaturated triosmium 5,6-benzoquinoline complex is treated with phosphanes[16a] and when the benzo ring of the unsaturated quinoline complex is dearomatized by nucleophilic addition followed by acid quenching.[16,18] For comparison purposes, the longest Os−C_{vinyl} distances in these complexes are in the range 2.3−2.5 Å,[16,18] being >0.2 Å shorter than the Os(1)−C(3) distance of compound **1**.

A reviewer of this work suggested that, according to a work of Arce et al.,[19] compound **1** could be considered as a 48-electron saturated species if the bridging naphthyl fragment acts as a 3-electron donor through only the C(2) atom. In Arce's report, a phenyl group that spans two metal atoms through only one C atom (η^1) is assigned as a 3-electron-donor ligand.[19] Apart from that work, all the remaining examples in which aryl groups behave as 3-electron donor bridging ligands display such groups coordinated in σ−π,μ-η^2-vinyl type mode.[16,18,20] In our case, a weak σ−π,μ-η^2-vinyl type interaction of the naphthyl fragment is observed in the solid state.

To summarize the issue of the unsaturation of compound **1**, there is a substantial amount of empirical evidence that supports a considerable degree of unsaturation: its fast reactions with donors, its green color (as other unsaturated triosmium clusters[16]), and its X-ray structure. The last piece of evidence clearly indicates that the metalated carbon atom of the naphthalene ring is the only carbon atom that interacts strongly with the osmium atoms. For a neat 46-electron species, one would expect that the naphthalene fragment would be perpendicular to the metal triangle, as in Rosenberg's compounds,[16] but this is not the case, as shown clearly in Figure 1b. Our explanation for this fact is that the leaning is caused by a weak π-interaction of the naphthalene C(2)−C(3) double bond with Os(1). The driving force for such an interaction would be that it partially relieves the unsaturation of the complex. Therefore, in our opinion, compound **1** is not a 46- nor a 48-electron species but has an electron count greater than 46 but smaller than 48, thus being an unsaturated species (electron count smaller than 48 for a trinuclear cluster).

The ruthenium acetonitrile complex $[Ru_3(MeCN)_2(CO)_{10}]$ did not react in the same way as its osmium analogue when it was treated with H_2binam. No reaction occurred in THF at room temperature. Upon heating to reflux temperature, $[Ru_3(MeCN)_2(CO)_{10}]$ decomposed into $[Ru_3(CO)_{12}]$ instead of reacting with H_2binam. Upon prolonged heating (refluxing THF, >2 h), $[Ru_3(CO)_{12}]$ reacted with H_2binam to give a brownish yellow solution. When this solution was evaporated to dryness, the solid residue, probably of polymeric nature, could not be redissolved and was not investigated further. It has been reported that the reactions of $[Ru_3(CO)_{12}]$ with 1,2-diaminobenzene[12e,21] and 1,8-diaminonaphthalene[12f,21] also afford polymeric products under similar reaction conditions.

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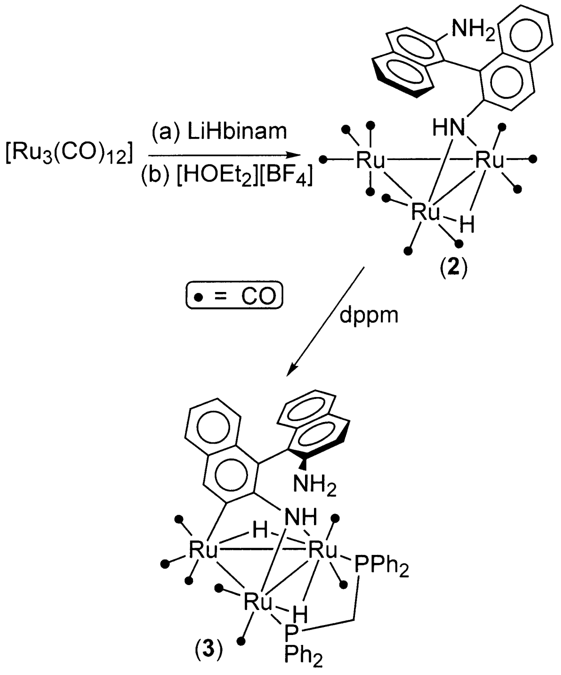
Scheme 2. Synthesis of Compounds 2 and 3



In an additional attempt to make a triruthenium derivative of H_2binam, $[Ru_3(CO)_{12}]$ was treated with the lithium salt LiHbinam. A smooth reaction was observed in THF at room temperature (2 h) that led to a very air-sensitive, dark red, anionic derivative, which was not isolated. Most probably, this anionic complex is $[Ru_3(\mu\text{-}\eta^1\text{-Hbinam-}N)(\mu\text{-CO})_3(CO)_7]^-$, by comparison of its IR spectrum with those of $[Ru_3(\mu\text{-}\eta^2\text{-Opy-}N,O)(\mu\text{-CO})_3(CO)_7]^-$ (HOpy = 2-pyridone),[22] $[Ru_3(\mu\text{-}\eta^1\text{-N=CPh}_2\text{-}N)(\mu\text{-CO})_3(CO)_7]^-$,[23] and $[Ru_3(\mu\text{-}\eta^2\text{-dmpz-}N,N)(\mu\text{-CO})_3(CO)_7]^-$ (Hdmpz = 3,5-dimethylpyrazole),[24] which contain 3-electron-donor ligands. Protonation of this dark red solution led to the neutral hydrido derivative $[Ru_3(\mu\text{-H})(\mu\text{-}\eta^1\text{-Hbinam-}N)(CO)_{10}]$ (**2**; Scheme 2), which was isolated as an orange solid. Kaesz was the first to observe that the attack of $[Ru_3(CO)_{12}]$ by anionic nucleophiles X^- (amido groups, halides, etc.) may result in the formation of anionic derivatives $[Ru_3(\mu\text{-X})(CO)_{10}]^-$, which can be subsequently protonated to give $[Ru_3(\mu\text{-H})(\mu\text{-X})(CO)_{10}]$.[25] We have previously reported that the compounds $[Ru_3(\mu\text{-H})(\mu\text{-}\eta^1\text{-N=CPh}_2\text{-}N)(CO)_{10}]$[23] and $[Ru_3(\mu\text{-H})(\mu\text{-}\eta^2\text{-dmpz-}N,N)(CO)_{10}]$[24] cannot be made by reaction of $[Ru_3(CO)_{12}]$ with the corresponding neutral ligand precursors but can be conveniently prepared by anionic routes analogous to that used for the synthesis of compound **2**. Curiously, it has been reported that the thermal reaction of aniline with $[Ru_3(CO)_{12}]$ gives the amido-bridged derivative $[Ru_3(\mu\text{-H})(\mu\text{-}\eta^1\text{-NHPh-}N)(CO)_{10}]$ among other products.[26]

The composition of compound **2** was confirmed by its microanalysis and FAB mass spectrum. Its DEPT ^{13}C and ^1H NMR spectra showed peaks corresponding to 12 CH groups, thus ruling out the possibility of a C-metalation. In addition, the $^{13}C\{^1H\}$ NMR spectrum also displayed 8 quaternary C and 10 *C*O resonances. The resonances of the hydride, N*H*, and N*H*$_2$ groups were observed as singlets at −12.66, 6.42, and 3.76 ppm, respectively. All these data strongly support the structure depicted for compound **2** in Scheme 2, which is comparable to that of other analogous,[27] X-ray diffraction characterized[27c−e] $[Ru_3(\mu\text{-H})(\mu\text{-}\eta^1\text{-NHR-}N)(CO)_{10}]$ complexes. It should be noted that the R group of the bridging amido fragment of all these complexes is in an exo disposition with respect to the metal triangle, probably to minimize steric interactions.

The C-metalation of the Hbinam ligand of compound **2** was attempted. However, no reaction was observed when it was heated in toluene at reflux temperature for 1 h or irradiated with UV light for 2 h. It seems that the reaction conditions used are too mild to overcome the activation energy of the ligand rearrangement that would facilitate the *C*-metalation process, since in **2**, as commented above, the naphthalene fragment attached to the bridging N atom adopts an exo disposition with respect to the metal triangle. Therefore, we decided to make some phosphane derivatives of **2**, expecting that they might undergo C-metalation processes of the Hbinam ligand under conditions milder than those required by **2**.

The asymmetry of the Hbinam ligand of **2**, in addition to the fact that both ruthenium atoms attached to the bridging nitrogen atom are likewise eager to undergo carbonyl substitution processes, accounts for the observation that the reactions of this complex with triphenylphosphane led to inseparable mixtures of compounds, regardless of the ratio of the reactants (1:1 to 1:3) and the reaction conditions (60−110 °C).

However, treatment of compound **2** with 1 equiv of bis(diphenylphosphanyl)methane (dppm), in THF at reflux temperature, allowed the isolation of $[Ru_3(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-binam-}C,N)(\mu\text{-}\eta^2\text{-dppm-}P,P)(CO)_7]$ (**3**; Scheme 2).

Complex **3** was characterized by an X-ray diffraction study (Figure 2). A selection of interatomic distances is given in Table 2. The metal triangle is capped by a doubly C- and N-metalated binam ligand in such a way that the C^3 carbon atom C(2) is σ-bonded to a metal atom and the NH fragment spans the edge defined by the two remaining metal atoms. In this case, the plane containing the coordinated naphthalene fragment is perpendicular to the trimetallic plane (dihedral angle 87.34(7)°). The dihedral angle between the planes of both naphthalene fragments is 83.0(1)°. A dppm ligand spans the same metallic edge as the NH fragment through both phosphorus atoms. The ligand shell is

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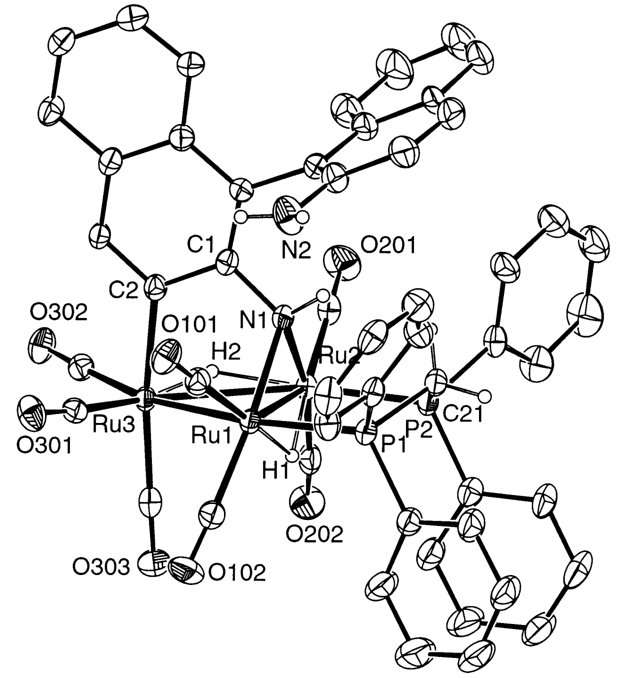


Figure 2. Molecular structure of compound **3** (50% probability level, aromatic H atoms omitted for clarity).

Table 2. Selected Interatomic Distances (Å) in Complex 3

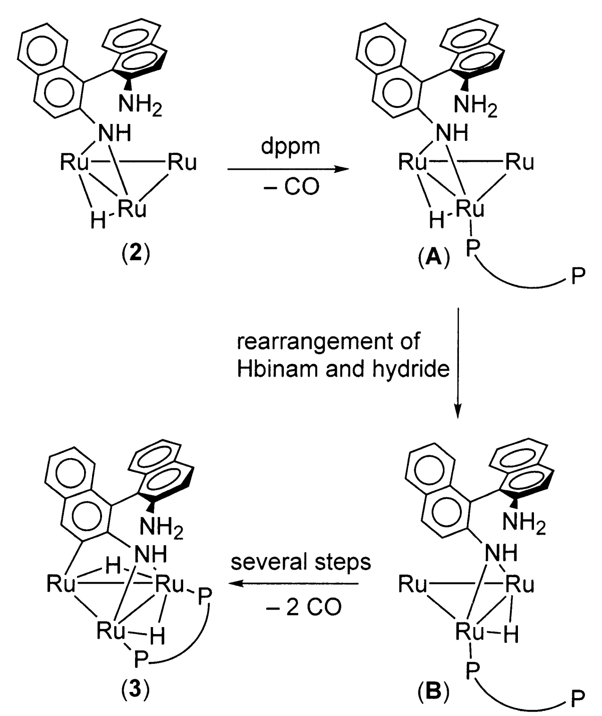
Ru(1)−Ru(2)	2.7840(5)	Ru(1)-Ru(3)	2.7752(5)
Ru(2)−Ru(3)	2.9694(5)	Ru(1)−P(1)	2.351(1)
Ru(1)−N(1)	2.139(4)	Ru(2)−P(2)	2.347(1)
Ru(2)−N(1)	2.136(4)	Ru(3)−C(2)	2.113(5)
P(1)−C(21)	1.843(5)	P(2)−C(21)	1.843(5)
C(1)−N(1)	1.433(6)	C(1)−C(2)	1.438(6)

completed by two hydride ligands and seven carbonyl groups. Thus, the complex is a coordinatively saturated 48-electron species.

The solution IR and NMR spectra of **3** confirm that in solution the complex maintains the same molecular structure as in the solid state. The IR spectrum shows only terminal CO ligands. The asymmetry of the complex is reflected by the observation of two doublet resonances in the $^{31}P\{^1H\}$ NMR spectrum (5.7 and −7.3 ppm, $J_{P-P} = 110.5$ Hz), corresponding to the phosphorus atoms of the dppm ligand. In addition to the resonances of the C*H* and C*H*$_2$ protons, the ^1H NMR spectrum also shows two singlet resonances, assignable to the N*H* (4.83 ppm) and N*H*$_2$ (2.75 ppm) protons, and two more complicated resonances (−11.65 and −13.64 ppm, both ddd), assignable to the hydride protons (they couple to each other and to both phosphorus atoms).

In the process that leads to complex **3** from **2** and dppm, the coordination of the dppm ligand should occur in an early reaction stage, prior to the C-metalation step, because complex **2** alone does not undergo C-metalation under thermal or photochemical conditions (vide supra). In Scheme 3, we propose that complex **2** reacts first with dppm to give an intermediate (**A**) which is prone to isomerize under the reaction conditions into a species having the naphthalene fragment in an endo disposition with respect to the metal triangle (**B**). We propose that this isomerization process should involve the migration of the bridging amido group from a metal−metal edge to another, rather than the inversion of the configuration of the nitrogen atom. In fact, such a migration process should be more influenced by the presence of certain ligands on the metal core than the inversion of the nitrogen atom. Therefore, if compound **2** does not undergo a nitrogen inversion under particular thermal conditions, neither should a phosphane derivative of **2**. We also propose that the intermediate **A** has a pendant monocoordinated dppm ligand, because if the bidentate coordination of the dppm ligand occurs before the migration of the bridging amido fragment, the P atoms of the dppm ligand should be attached to the same Ru atoms as the amido fragment,[23,28] and this, after the migration of the amido ligand, would end in a final complex in which the amido fragment and the dppm ligand would not span the same Ru−Ru edge. Before ending in complex **3**, intermediate **B** should undergo easy C−H bond activation, phosphorus coordination, and CO elimination processes, the order of which remains unknown.

Scheme 3. Initial Steps of the Reaction Pathway that Leads to Complex 3 from Complex 2 and dppm[a]



[a] Carbonyl ligands are omitted for clarity.

In ruthenium chemistry, we are not aware of previous examples of C-metalated aromatic amines. However, some triosmium complexes structurally related to compound **3**, containing doubly C- and N-metalated aromatic amines, have been reported.[12c,14,15]

Concluding Remarks

This work describes the synthesis of the first trinuclear cluster derivatives of H_2binam and the first C-metalated complexes of this ligand. Complex **3** also is an unprecedented example of a C-ruthenated aromatic amine.

The synthesis and characterization of the unsaturated compound **1** have shown that, in ligand-bridged trio-

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smium compounds, the existence of a pyridinic nitrogen within the bridging ligand (all the previous examples are of this type[15-18]) is not a must for the formation of the electron-deficient bonding mode, since it can also be formed with aromatic amines.

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (THF, Et_2O, hydrocarbons) or CaH_2 (dichloromethane) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen, using Schlenk−vacuum-line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region) and spot TLC (silica gel). Racemic H_2binam[29] and $[Os_3(MeCN)_2(CO)_{10}]$[30] were prepared as described previously; the remaining reagents, including (*R*)-(+)-H_2binam (ee >99%, Fluka), were purchased from commercial suppliers. IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. NMR spectra were run at room temperature on a Bruker DPX-300 instrument, using 85% H_3PO_4 (external, δ 0) or the dichloromethane solvent resonance (internal, δ 5.35 for ^1H and 53.5 for ^{13}C) as standards. Microanalyses were obtained from the University of Oviedo Analytical Service. Positive FAB-MS were obtained from the University of Santiago de Compostela Mass Spectrometric Service; data given refer to the most abundant molecular ion isotopomer.

$[Os_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}Hbinam\text{-}N,C)(CO)_9]$ (1). A solution of H_2binam (33 mg, 0.115 mmol) and $[Os_3(MeCN)_2(CO)_{10}]$ (90 mg, 0.096 mmol) in THF (40 mL) was heated at reflux temperature for 2 h. The color changed from yellow to brown. The solvent was removed under reduced pressure, and the resulting residue was dissolved in a minimal amount of dichloromethane. The solution was separated by column chromatography (silica gel, 2 × 15 cm, packed in hexane). Hexane−dichloromethane (4:1) eluted two minor yellow bands. Hexane−dichloromethane (3:2) eluted the major band, which afforded compound **1** as a greenish brown solid after solvent removal (41 mg, 39%). Anal. Calcd for $C_{29}H_{16}N_2O_9Os_3$ (M_r = 1106.68): C, 31.46; H, 1.45; N, 2.53. Found: C, 31.43; H, 1.60; N, 2.43. MS (*m*/*z*): 1108 [M^+]. IR (CH_2Cl_2): ν_{CO} 2077 (m), 2045 (s), 2022 (s), 1986 (m), 1966 (m, sh), 1939 (w, sh) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.2−6.8 (m, 11 H, C*H*), 6.10 (d, *J* = 11.5 Hz, 1 H, N*H*$_2$), 5.12 (d, *J* = 11.5 Hz, 1 H, N*H*$_2$), 3.89 (s, 2 H, N*H*$_2$), −14.95 (s, 1 H, μ-*H*).$^{13}C\{^1H\}$ NMR (DEPT, CD_2Cl_2): δ 185.1, 184.5, 182.1, 181.5, 180.5, 178.4 (×2), 176.9, 176.5 (9 *C*Os); 158.1, 143.0, 133.6, 132.2, 128.3, 128.2, 121.3, 110.3, 95.1 (9 *C*s); 131.7, 130.8 (x 2), 130.1, 128.8, 128.5, 127.1, 126.9, 124.0, 123.2, 118.9 (11 *C*Hs).

$[Ru_3(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}Hbinam\text{-}N)(CO)_{10}]$ (2). A hexane solution of BuLi (0.90 mL, 1.6 M, 1.440 mmol) was dropwise injected onto a stirred cold (−78 °C) solution of H_2binam (405 mg, 1.423 mmol) in THF (60 mL). The color changed from colorless to yellow. The solution was slowly warmed to room temperature before solid $[Ru_3(CO)_{12}]$ was added (900 mg, 1.408 mmol). The color changed from orange to dark red. After the mixture was stirred for 2 h at room temperature, a solution of $[HOEt_2][BF_4]$ in diethyl ether (1.50 mL, 1 M, 1.500 mmol) was dropwise injected. The color changed from red to orange-yellow. The solvent was removed under reduced pressure, and the resulting residue was dissolved in a minimal amount of dichloromethane. The solution was separated by column chromatography (silica gel, 2 × 15 cm, packed in hexane). Hexane eluted a small amount of $[Ru_3(CO)_{12}]$. Hexane−dichloromethane (4:1) eluted the major band, which afforded compound **2** as an orange solid after solvent removal (879 mg, 72%). Anal. Calcd for $C_{30}H_{16}N_2O_{10}Ru_3$ (M_r = 867.32): C, 41.52; H, 1.85; N, 3.22. Found: C, 41.43; H, 1.90; N, 3.15. MS (*m*/*z*): 869 [M^+]. IR (CH_2Cl_2): ν_{CO} 2099 (m), 2061 (s), 2048 (s), 2015 (s), 1998 (m, sh), 1984 (w, sh) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.2−6.8 (m, 12 H, C*H*), 6.42 (s, 1 H, N*H*), 3.76 (s, 2 H, N*H*$_2$), −12.66 (s, 1 H, μ-*H*). $^{13}C\{^1H\}$ NMR (DEPT, CD_2Cl_2): δ 206.8, 204.8, 200.2 (×2), 195.2, 193.8, 193.6, 193.5, 186.8 (×2) (10 *C*Os); 161.1, 143.7, 133.9, 132.0, 131.2, 129.0, 120.5 118.5 (8 *C*s); 131.8, 129.7, 128.7 (×2), 128.5, 127.8, 125.7, 125.4, 124.7, 123.1, 122.9, 118.5 (12 *C*Hs).

Table 3. Crystal, Measurement, and Refinement Data for $1\cdot0.5CH_2Cl_2$ and 3

	1·$0.5CH_2Cl_2$	**3**
formula	$C_{29}H_{16}N_2O_9Os_3\cdot0.5CH_2Cl_2$	$C_{52}H_{38}N_2O_7P_2Ru_3$
fw	1149.50	1167.99
cryst syst	monoclinic	triclinic
space group	$P2_1$ (No. 3)	$P\bar{1}$ (No. 2)
a, Å	8.415(5)	13.9445(5)
b, Å	12.852(6)	14.2229(5)
c, Å	15.277(8)	15.2432(5)
α, deg	90	86.964(2)
β, deg	100.04(6)	77.534(2)
γ, deg	90	63.183(2)
V, Å^3	1627(1)	2631.0(2)
Z	2	2
F(000)	1050	1164
D_{calcd}, g cm^{-3}	2.347	1.474
radiation (*λ*, Å)	Mo Kα (0.710 73)	Cu Kα (1.541 80)
μ, mm^{-1}	11.821	7.863
cryst size, mm	0.23 × 0.13 × 0.13	0.17 × 0.10 × 0.10
temp, K	293(2)	200(2)
θ limits, deg	2.46 to 26.00	2.97 to 68.64
h, *k*, *l* range	−10 to +10, −15 to +15, −18 to +18	0−16, −14 to +17, −17 to +18
no. of collected rflns	6918	34186
no. of unique rflns (R_{int})	6368 (0.081)	9665 (0.059)
no. of rflns with $I > 2\sigma(I)$	3638	8487
refinement method	full-matrix least-squares on F^2	
abs cor	RefDelf (XABS2)	
max/min transmissn	0.215/0.073	0.453/0.227
no. of restraints/params	1/210	2/613
GOF on F^2	1.011	1.157
final R1 (on *F*, $I > 2\sigma(I)$)	0.0604	0.0493
final wR2 (on F^2, all data)	0.1659	0.1674
Flack param	−0.04(3)	
max/min residuals, e Å^{-3}	1.610/−1.745	1.018/−1.419

$[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2\text{-}binam\text{-}C,N)(\mu\text{-}\eta^2\text{-}dppm\text{-}P,P)(CO)_7]$ (3). A solution of dppm (49 mg, 0.128 mmol) and compound **2** (100 mg, 0.115 mmol) in THF (40 mL) was heated at reflux temperature for 30 min. The color changed from orange to red. The solvent was removed under reduced pressure, and the resulting residue was dissolved in a minimal amount of dichloromethane. The solution was separated by column chromatography (silica gel, 2 × 15 cm, packed in hexane). Hexane−dichloromethane (4:1) eluted an orange band containing some starting material **2**. Hexane−dichloromethane (1:1) eluted the major band, which afforded compound **3** as a red solid after solvent removal (72 mg, 54%). Anal. Calcd for $C_{52}H_{38}N_2O_7P_2Ru_3$ (M_r = 1167.99): C, 53.40; H, 3.27; N, 2.39. Found: C, 53.60; H, 3.61; N, 2.50. MS (*m*/*z*): 1169 [M^+]. IR (CH_2Cl_2): ν_{CO} 2077 (w), 2057 (m), 2039 (s), 1995 (vs), 1971 (w, sh), 1939 (w, sh) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.2−6.2 (m, 31 H, C*H*), 4.83 (s, 1 H, N*H*), 3.84 (m, 1 H, C*H*$_2$), 2.75 (s, 2 H, N*H*$_2$), 2.55 (m, 1 H, C*H*$_2$), −11.65 (ddd, *J* = 17.2, 8.8, 1.5 Hz, 1 H, μ-*H*), −13.64 (ddd, *J* = 51.1, 5.0, 1.5 Hz, 1 H, μ-*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 5.7 (d, *J* = 110.5 Hz, 1 P), −7.3 (d, *J* = 110.5 Hz, 1 P).

X-ray Structures of Compounds $1\cdot0.5CH_2Cl_2$ and 3. Suitable crystals were obtained by slow evaporation of a CH_2Cl_2 solution of the enantiomer of **1** derived from (*R*)-(+)-H_2binam and by slow diffusion of pentanes into a CH_2Cl_2 solution of complex **3**. A selection of crystal and refinement data for both structures is given in Table 3. Diffraction data for **1**·$0.5CH_2Cl_2$ were collected on a Nonius CAD-4 diffractometer, with the $\omega-2\theta$ scan technique and a variable scan rate, using

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graphite-monochromated Mo Kα radiation. Lorentz and polarization corrections were applied. Diffraction data for **3** were collected on a Nonius Kappa-CCD diffractometer equipped with a 95 mm CCD camera on a κ-goniostat, using graphite-monochromated Cu Kα radiation. In both cases, data were reduced to F_o^2 values. The structures were solved by Patterson interpretation using the program DIRDIF-96.[31] Absorption corrections were performed using XABS2.[32] Isotropic and full-matrix anisotropic least-squares refinements were carried out using SHELXL-97.[33] For **1**·$0.5CH_2Cl_2$, the osmium and chlorine atoms were refined anisotropically. The remaining non-H atoms were refined isotropically because many of them were persistently nonpositive definite. The hydrogen atom positions of both NH_2 groups were geometrically calculated, and their coordinates and thermal parameters were fixed. The hydride atom position was calculated using the program XHYDEX,[34] and its coordinates and thermal parameters were fixed. All the remaining hydrogen atom positions were calculated and refined riding in their parent atoms. For **3**, all non-H atoms were refined anisotropically. The NH and NH_2 hydrogen atoms and the hydride atoms were located in the corresponding Fourier maps and were freely refined, except for the N−H distances of the NH_2 group, which were fixed. All the other hydrogen atom positions were geometrically calculated and refined riding on their parent atoms. Geometrical calculations were performed with PARST.[35] The molecular plots were made with the EUCLID program package.[36] The WINGX program system[37] was used throughout both structure determinations.

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Supporting Information Available: Tables of bond distances and angles, atomic coordinates, and anisotropic thermal parameters for compounds **1**·$0.5CH_2Cl_2$ and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020903W

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