

Electrophilic Activation of Osmium-Nitrido Corroles: The OsN Triple Bond as a π -Acceptor Metallaligand in a Heterobimetallic Os^{VI}N–Pt^{II} Complex

Anders Reinholdt, Abraham B. Alemayehu, Kevin J. Gagnon, Jesper Bendix,* and Abhik Ghosh*



Cite This: *Inorg. Chem.* 2020, 59, 5276–5280



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ABSTRACT: Presented herein is a first investigation of the chemical reactivity of osmium-nitrido corroles, which are known for their unusual thermal, chemical, and photochemical stability. Elemental chlorine perchlorinates the β -positions of the triarylcorrole but leaves the OsN unit untouched. The OsN unit is also unaffected by a variety of other electrophilic and nucleophilic reagents. Upon photolysis, however, the anion of Zeise's salt associates with the nitrido ligand to generate an Os^{VI}≡N–Pt^{II} complex. The very short OsN–Pt linkage [1.895(9)–1.917(8) Å] and the downfield ¹⁹⁵Pt NMR resonance (–2702 ppm) suggest that the OsN corrole acts as a π -accepting ligand toward the Pt(II) center. This finding represents a rare example of the successful photochemical activation of a metal–ligand multiple bond that is too kinetically inert to exhibit any appreciable reactivity under thermal conditions.

The 5d metallocorroles are size-mismatched assemblies of a large 5d transition metal ion and sterically constrained, macrocyclic corrole ligands.^{1,2} Remarkably, in spite of the steric mismatch inherent in their structures, the majority of such complexes are unusually stable, both thermally and photochemically.^{3–12} In addition, many of them exhibit room-temperature NIR phosphorescence,^{13–18} which has led to applications in oxygen sensors,^{14–16} photodynamic therapy,^{17,19} and dye-sensitized solar cells.¹⁷ Their chemical reactivity, in contrast, remains poorly explored. Thus, gold triarylcorroles have been β -perbrominated^{20,21} and certain M^VO corroles have been derivatized to the corresponding Viking-helmet dichlorides, that is, M^VCl₂ corroles.²² In this communication, we document two complementary avenues for the further elaboration of osmium(VI)-nitrido corroles (Scheme 1). One involves direct reaction with elemental chlorine, affording a facile route to Os^{VI}N octachlorocorroles. The second is more innovative and is based on the use of the Os^{VI}N moiety as a π -acceptor ligand in the formation of an Os^{VI}N–Pt^{II} heterobimetallic complex, as described herein.

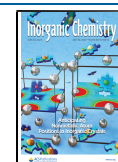
Unfortunately, β -perbromination of Os^{VI}N triarylcorroles proved difficult: many hours of exposure to elemental bromine led only to a mixture of the hexa-, hepta-, and octa-brominated products. Although steric congestion in the products is a tempting explanation, we believe that the high-oxidation-state Os exerts the key deactivating influence on the corrole macrocycle. In contrast, β -perchlorination of Os^{VI}N corroles occurred readily upon exposure to elemental chlorine at room temperature for several minutes. Since we were primarily interested in metal-centered reactivity, we characterized and structurally analyzed only one β -perchlorinated product, Os[Cl₈TPC](N) (1, Table S1 and Figure 1). The Os–N_{corrole} (1.98–2.00 Å) and Os–N_{nitrido} (1.63–1.64 Å) distances proved similar to those found in β -unsubstituted Os^{VI}N corroles.⁶ Both the Soret and Q bands of Os[Cl₈TPC](N)

were found to be significantly red-shifted relative to the starting material, reflecting the electronic effect of β -octachlorination (Figure 2).

Osmium-nitrido complexes represent the border between nucleophilic and electrophilic reactivity,^{23–36} which are characteristic of early and late transition metal-nitrido complexes, respectively. Yet, a preliminary examination of the reactivity of the Os^{VI}N corroles with both nucleophilic (PPh₃) and electrophilic reagents (MeI, I₂) failed to yield the expected nitride-derived products. Taking a cue from recent uses of nitride^{37–39} and carbide^{40,41} complexes as novel π -acceptor ligands, we attempted to deploy Os^{VI}N triarylcorroles in a similar manner. No transformation, however, was observed upon exposure to electron-rich transition metal complexes with labile ligands, including AuCl(tht), [RhCl(cod)]₂, [IrCl(cod)]₂, and the Zeise's salt analogue (AsPh₄)[Pt(C₂H₄)Cl₃] (tht = tetrahydrothiophene, cod = 1,4-cyclooctadiene).^{37–41} Indeed, even upon prolonged heating in bromoform (100 °C, 20 h), the Os^{VI}N corroles and (AsPh₄)[Pt(C₂H₄)Cl₃] failed to react. As a last resort, we attempted to activate Os^{VI}N corroles photochemically (λ = 365 nm), inspired in part by the reports of photolytic activation of Os^{VI}N complexes leading to N–N coupling⁴² and C–H functionalization.⁴³ The results proved promising, especially with the electronegatively substituted tris(*p*-trifluoromethylphenyl)corrole complex Os-[TpCF₃TPC](N). According to NMR analysis, UV irradiation with [RhCl(cod)]₂ over 18 h led to low levels (7%) of conversion to Os[TpCF₃TPC](N)–Rh(cod)Cl, as evidenced

Received: March 2, 2020

Published: March 31, 2020



Scheme 1. Electrophilic Activation of OsN Corroles

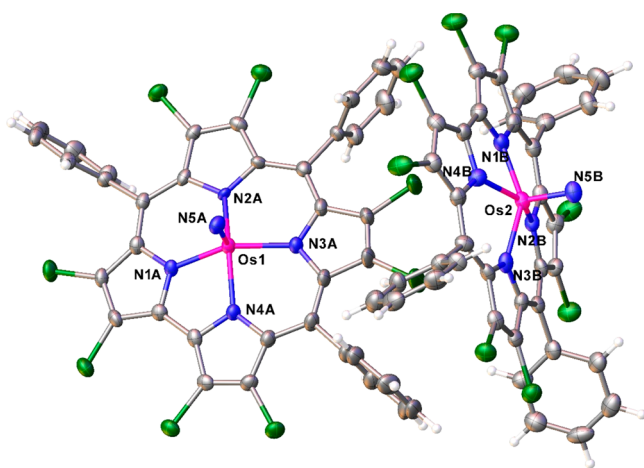
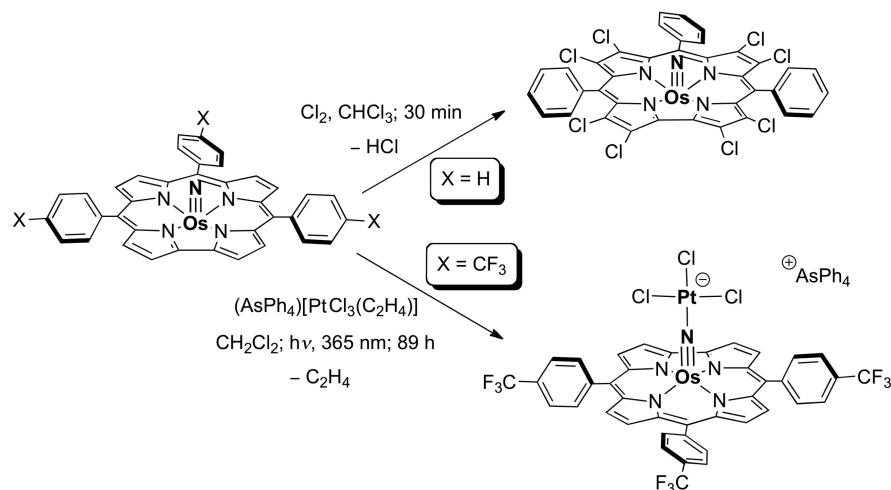


Figure 1. Thermal ellipsoid (50%) plot for $\text{Os}[\text{Cl}_8\text{TPP}](\text{N})$ (**1**). Selected distances (\AA): Os1–N1A 1.986(5); Os1–N2A 1.999(4); Os1–N3A 2.004(5); Os1–N4A 1.979(5); Os1–N5A 1.630(6); Os2–N1B 1.991(5); Os2–N2B 1.990(5); Os2–N3B 1.994(5); Os2–N4B 1.990(5); Os2–N5B 1.642(5).

by an upfield shift of the β -hydrogen resonances of the corrole. Much better yields of $(\text{AsPh}_4)\{\text{Os}[\text{TpCF}_3\text{TPC}](\text{N})-\text{PtCl}_3\}$ (**2**, 30% conversion after 20 h) were obtained with $(\text{AsPh}_4)-[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ in dichloromethane. The retention of the ^1H resonance from unconverted $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$ ($^2J_{\text{Pt-H}} \approx 60$ Hz) suggests that the photolytic reaction proceeds via activation of the $\text{Os}^{\text{VI}}\text{N}$ corrole, as opposed to a scenario in which the ethylene ligand dissociates to generate an activated platinum(II) center.

The X-ray structure of **2** (Table S1 and Figure 3) revealed a slight elongation (~ 0.02 \AA) of the $\text{Os}\equiv\text{N}$ triple bond relative to the starting complex.⁶ Comparison of the different Pt–Cl distances showed that the nitride ligand in **2** exerts a slightly weaker *trans* influence than chloride (2.295 versus 2.318 \AA), indicating that the $\text{Os}^{\text{VI}}\text{N}$ corrole is a weak σ -donor. Remarkably, the $\text{OsN}-\text{Pt}$ bond proved to be much shorter (~ 1.90 \AA) than those in most other $[\text{Pt}(\text{L})\text{Cl}_3]^-$ anions with *N*-donor ligands (Table S2), indeed among the shortest 1% in the Cambridge Structural Database (Figure S9). Such a short Pt–N bond suggests partial multiple-bond character, consistent with the $\text{Os}\equiv\text{N}$ triple bond acting as a π -acceptor

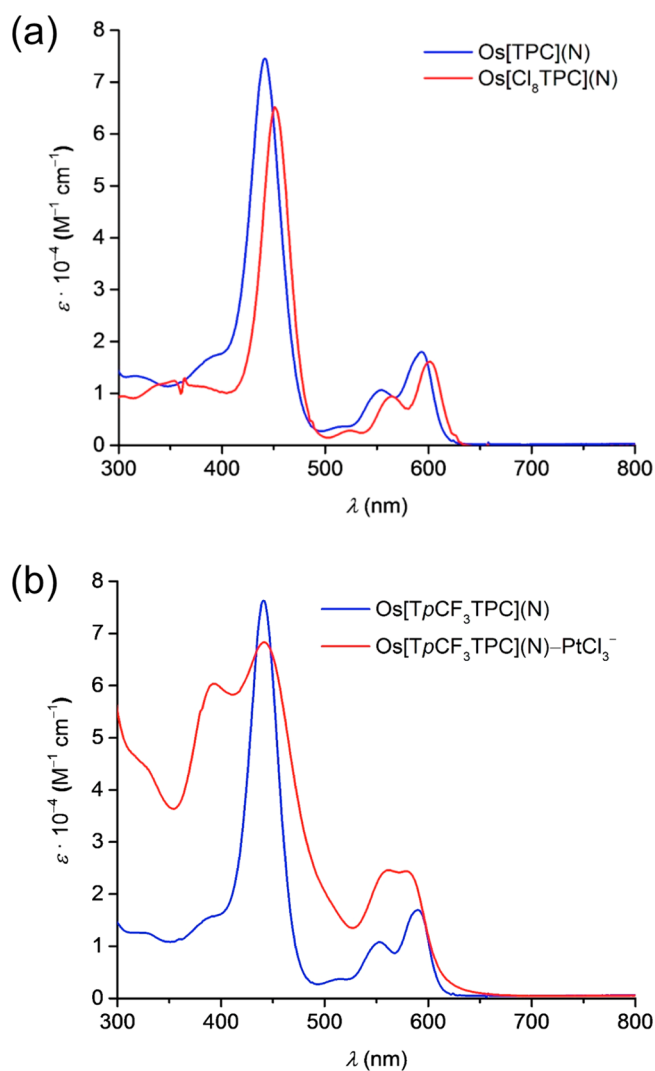


Figure 2. Comparative UV–vis spectra in dichloromethane: (a) $\text{Os}[\text{Cl}_8\text{TPC}](\text{N})$ (**1**) and $\text{Os}[\text{TPC}](\text{N})$; (b) $\text{Os}[\text{TpCF}_3\text{TPC}](\text{N})$ and $(\text{AsPh}_4)\{\text{Os}[\text{TpCF}_3\text{TPC}](\text{N})-\text{PtCl}_3\}$ (**2**).

ligand toward Pt(II), which in turn is consistent with dramatic changes in the UV–vis spectrum upon Pt(II) coordination (Figure 2) as well as with ^{195}Pt NMR spectroscopy.^{44,45} In the

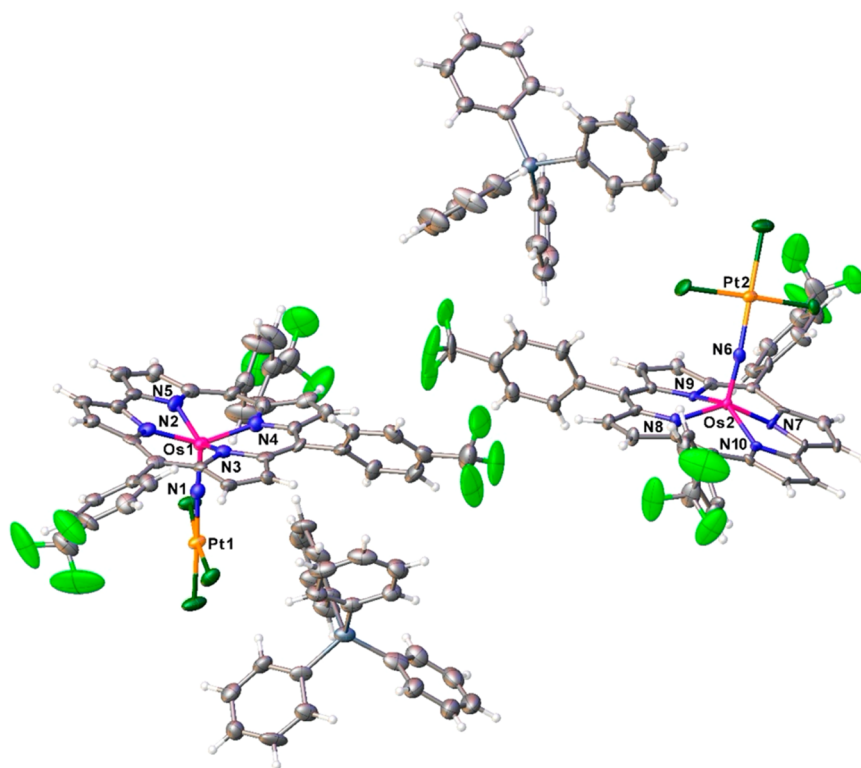


Figure 3. Thermal ellipsoid (30%) plot for $(\text{AsPh}_4)\{\text{Os}[\text{TpCF}_3\text{TPC}](\text{N})\text{-PtCl}_3\}$ (**2**). Selected distances (Å): Os1–N1 1.664(9), Os1–N2 1.979(9), Os1–N3 1.988(8), Os1–N4 1.978(9), Os1–N5 1.969(8), Pt1–N1 1.895(9), Os2–N6 1.656(8), Os2–N7 1.969(8), Os2–N8 1.982(8), Os2–N9 1.978(7), Os2–N10 1.973(7), Pt2–N6 1.917(8).

latter method, a π -backbonding ligand results in a decrease of the electron density at the platinum nucleus and thereby a downfield shift of the ^{195}Pt resonance. Complex **2** exhibits a ^{195}Pt NMR chemical shift at -2702 ppm, downfield of the starting material $(\text{AsPh}_4)[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ at -2751 ppm. To gain a wider frame of reference, we also recorded the ^{195}Pt NMR spectrum for a carbide-bridged analog of **2**, $(\text{AsPh}_4)[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}\text{-PtCl}_3]$, which exhibits a strongly downfield-shifted ^{195}Pt NMR resonance at -2499 ppm.⁴⁰ Thus, the π -backbonding strength of L in the $(\text{AsPh}_4)[\text{Pt}(\text{L})\text{Cl}_3]$ family increases in the order $\text{L} = \text{C}_2\text{H}_4 < \text{Os}[\text{TpCF}_3\text{TPC}](\text{N}) < (\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}$, thereby establishing $\text{Os}[\text{TpCF}_3\text{TPC}](\text{N})$ as a moderately strong π -backbonding ligand. Differences in π -backbonding between $\text{M}\equiv\text{C}$ and $\text{M}\equiv\text{N}$ metallaligands presumably impact their relative lability; thus, $\text{Ru}\equiv\text{C}$ ligands are less prone to dissociate from Pt(II) centers than $\text{Cr}\equiv\text{N}$ ligands.⁴⁶

In conclusion, $\text{Os}^{\text{VI}}\text{N}$ corroles are surprisingly inert toward both nucleophilic and electrophilic reagents. Elemental chlorine perchlorinates the β -positions of the corrole but leaves the central OsN unit untouched. Only upon photolysis does the OsN unit react with the Zeise anion, affording a heterobinuclear $\text{Os}\equiv\text{N}\text{-Pt}$ complex. Although mechanistic details remain to be elucidated, this study may well provide a rare example of photochemical activation of a metal–ligand multiple bond that is too inert to react thermally with common nucleophiles and electrophiles. That in turn would imply that the common classification of metal–ligand multiple bonds as nucleophilic, electrophilic, or ambiphilic may provide an incomplete picture of their reactivity; that is, excited state reactivity may differ dramatically from ground state reactivity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00654>.

Synthetic procedures, spectroscopic data, crystallographic protocols and data, and Cambridge Structural Database analyses (PDF)

Accession Codes

CCDC 1985901–1985902 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

Jesper Bendix – Department of Chemistry, University of Copenhagen, DK-2100 Copenhagen, Denmark; orcid.org/0000-0003-1255-2868; Email: bendix@kiku.dk

Abhik Ghosh – Department of Chemistry, UiT – The Arctic University of Norway, N-9037 Tromsø, Norway; orcid.org/0000-0003-1161-6364; Email: abhik.ghosh@uit.no

Authors

Anders Reinholdt – Department of Chemistry, University of Copenhagen, DK-2100 Copenhagen, Denmark; orcid.org/0000-0001-6637-8338

Abraham B. Alemayehu – Department of Chemistry, UiT – The Arctic University of Norway, N-9037 Tromsø, Norway; orcid.org/0000-0003-0166-8937

Kevin J. Gagnon – Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720-8229, United States

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.inorgchem.0c00654>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Research Council of Norway (Grant 262229), the Carlsberg Foundation (Grant CF18-0613), the Independent Research Fund Denmark (Grant 9036-00015B), and the Advanced Light Source, a DOE Office of Science User Facility, under Contract No. DE-AC02-05CH11231.

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