A Theoretical Search for Terminal Carbides and d-Block–p-Block Quadruple Bonds

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Abstract. Exploratory scalar-relativistic DFT calculations (B3LYP*-D3/ZORA-STO-TZ2P) have been used to examine the stability and bonding of pseudotetrahedral Group 8 (Fe, Ru, Os) and Group 9 (Co, Rh, Ir) terminal carbide complexes with tripodal tris(N-heterocyclic-carbene) supporting ligands. The complexes examined are all charge-neutral, with d_δ^4 ground states. The complexes exhibit relatively low adiabatic ionization potentials in the 4.3-5.9 eV range and sizable adiabatic singlet-triplet gaps in the 0.9-1.6 eV range. Furthermore, all the complexes exhibit near-zero or strongly negative electron affinities, indicating high reductive stability. These calculated results suggest that, once successfully synthesized, the majority of the complexes examined should be isolable and moderately stable. As far as bonding in the metal-carbido moiety is concerned, NBO analyses suggest a triple bond, with a 2s-like lone pair on the carbido carbon.

Keywords: terminal carbide, carbide, quadruple bond, DFT

INTRODUCTION

Transition metal terminal carbides are exceedingly rare.[1] The handful of examples known to date hail from Groups 6 and 8, including [{N(R)Ar}$_3$Mo($\equiv$C:)]$^-$ (Tp* = 3,5-dimethyltris(pyrazolyl)borate) and [Tp*(CO)$_2$M($\equiv$CLi)] (M = W, Mo),[2,3,4,5] [M($\equiv$C:)(L)$_2$(X)$_2$] (M = Ru, Os),[6,7,8,9] and [P$_2$Mo($\equiv$C:)(CO)]$^{+,0,-}$ (P2 = a terphenyl-diphosphine ligand).[10,11] For square-pyramidal and octahedral complexes, a "carbido wall" (analogous to the oxo wall) appears to apply at a d-electron of 2, corresponding to a d$_\delta^2$ electronic configuration. Thus, an Ir(VII)-carbido corrole has been postulated as a stable species. Higher d-electron counts of up to 4 are conceivable for pseudotetrahedral complexes, corresponding to a d$_\delta^4$ electronic configuration. Little, however, is known about the actual stability of such complexes or about their excited-state architectures. Our curiosity about this question was further piqued by reports of quadruple binding in the diatomic molecule RhB[12,13] and subsequently in several additional diatomics.[14,15] Might an isoelectronic quadruple-bonded metal-carbide fragment be isolable in the form of a synthetic complex?[16,17] To shed light on the question, we have examined a series of d^4 pseudotetrahedral tris(*N*-heterocyclic-carbene) transition metal carbides and nitrides with density functional theory (DFT) calculations. The nitrido complexes examined are closely related to stable, experimentally well-characterized systems[18,19,20,21] and have been included here as calibration for our calculations on the speculative carbido systems. Based on their singlet-triplet gaps and electron affinities, several of the terminal carbides examined are indeed expected to be thermodynamically stable and hence worthwhile synthetic targets.[22,23]

M^V(L1)(C)
"trisNHCborate(−1)"

M^{IV}(L2)(C)
"trisNHCmethane(0)"

B

C

M = Co, Rh, Ir

M = Fe, Ru, Os
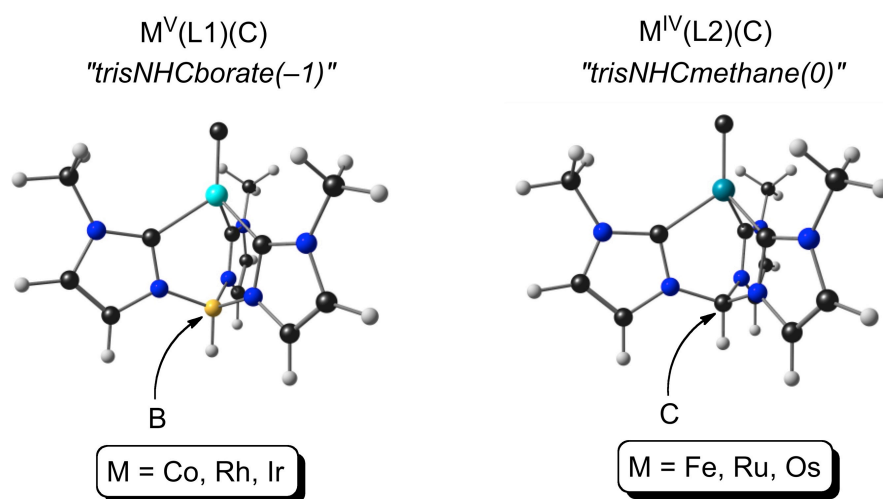
Scheme 1. Terminal carbides studied in this work.

Table 1. Selected calculated results on the molecules studied. L_{ax} = C or N; $C_{carbene}$ refers to the carbene center in the tris(carbene) ligand; B.O. refers to the Mayer bond order.

	d(M-L_{ax}) (Å)	d(M-$C_{carbene}$) (Å)	θ(L_{ax}-M-$C_{carbene}$) (°)	IP (eV)	EA (eV)	E_{S-T} (eV)	B.O.
Co(L1)(C)	1.516	1.920	121.5	5.623	-0.185	0.892	2.686
Rh(L1)(C)	1.627	2.104	126.0	5.849	-0.393	1.444	2.751
Ir(L1)(C)	1.672	2.067	124.9	5.698	-0.031	1.210	2.755
Fe(L1)(N)	1.498	1.915	122.2	5.406	0.013	0.479	2.738
Ru(L1)(N)	1.619	2.064	126.3	5.666	-0.177	1.161	2.729
Os(L1)(N)	1.655	2.038	125.0	5.566	0.133	1.020	2.696
Fe(L2)(C)	1.527	1.876	122.0	4.343	-0.976	1.305	2.835
Os(L2)(C)	1.691	2.015	124.8	4.843	-0.818	1.459	2.822
Ru(L2)(C)	1.649	2.047	126.0	4.706	-0.888	1.650	2.871

RESULTS AND DISCUSSION

Two different tripodal tris(carbene) ligands were investigated, an anionic ligand L1 with a BH anchor (trisNHCborate) and a neutral ligand L2 with a CH anchor (trisNHCmethane). Scheme 1 depicts the molecules studied and Table 1 presents key DFT (B3LYP*-D3/ZORA-STO-TZ2P) results. The results encompass four major experimentally observable quantities, namely bond distances and angles and adiabatic ionization potentials, electron affinities, and singlet-triplet gaps. None of the species examined evinced unduly small HOMO-LUMO gaps (or singlet-triplet gaps) so no pressing need was apparent for the deployment of multiconfigurational methods.

As expected for terminal carbides, our calculations predict short axial M-$C_{carbido}$ bonds, which hover around 1.5 Å for Fe and Co, around 1.64 Å for Ru and Rh, and around 1.68 Å for Os and Ir. These distances are only slightly longer (by 0.01-0.02 Å) than the axial M-$N_{nitrido}$ complexes calculated for the M(L1)(N) series. In an interesting reversal, the M-C single bonds involving the ligands L1 and L2 are slightly longer for Ru and Rh than their 5d congeners Os and Ir, respectively. We have not examined the origin of this reversal, but Pyykkö's covalent radii[24,25,26] echo a similar effect. Thus, while the double- and triple-bond covalent radii of Ir (1.15 and 1.07 Å, respectively) are longer than those of Rh (1.10 and 1.06 Å, respectively), the single bond covalent radius of Ir (1.22 Å) is shorter than that of Rh (1.25 Å).

The complexes in the M(L1)(C) and M(L1)(N) series (M = Co, Rh, Ir) exhibit "healthy" (i.e., not unduly low) IPs in the 5-6 eV range that are consistent with their existence as stable compounds. The M(L2)(C) series (M = Fe, Ru, Os) does exhibit lower IPs in the 4-5 eV range, indicating a certain sensitivity to oxidation. By way of perspective, many electron-

rich but air-stable porphyrin-type molecules such as tetrabenzoporphyrin exhibit IPs in the 5-6 eV range.[27,28,29,30,31]
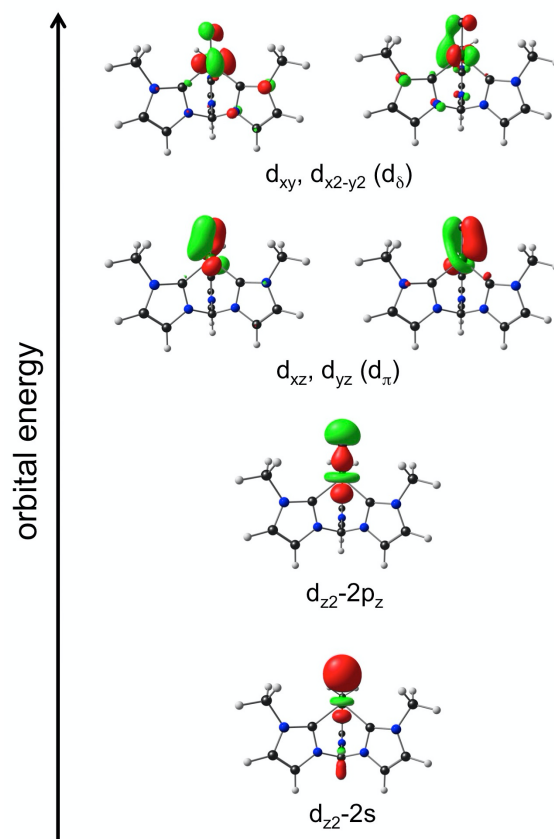

Figure 1. Selected occupied Kohn-Sham MOs for Os(L2)(C).

Interestingly, none of the compounds examined exhibits a significant adiabatic EA. In fact, the majority of them exhibit negative EAs and the molecules in M(L2)(C) series exhibit exceptionally large negative EAs for neutral molecules. In other words, these complexes are not expected to give rise to stable gas-phase anions and in solution are expected to exhibit unusually low reduction potentials. The compounds are thus all predicted to be reductively stable.

In light of frontier orbital theory,[32,33] HOMO-LUMO gaps and singlet-triplet gaps provide a popular and well-justified measure of a molecule's reactivity. The low calculated singlet-triplet gap of around 0.5 eV for Fe(L1)(N) is consistent with the relatively reactive nature of analogous compounds with stabilized, carbene-type species such as CO and isocyanides. Notably, an S-T gap of almost 0.9 eV is predicted for Co(L1)(C), while even higher S-T gaps > 1 eV are predicted for the other carbido complexes examined, strongly suggesting that these complexes should exist as stable compounds.

Pivoting to the question of metal-carbon quadruple bonding in the terminal carbides examined, four canonical MOs indeed exhibit significant M-$C_{carbido}$ bonding. These are the two $M(d_\pi)$-$C(p_\pi)$ π-bonding MOs, a predominantly d_{z2}-p_z–based σ-bonding MO, and a predominantly d_{z2}-2s-based σ-bonding MO (Figure 1). NBO analysis, however, indicates only three MOs with predominant M-$C_{carbido}$ bonding character, namely two π and one σ NBO, along with a 2s-like lone pair on the carbide carbon. The second σ-bond found in diatomics such as RhB[12–15] does not appear to survive in the presence of the strongly σ-donating triscarbene supporting ligand. The Mayer bond order for the M-$C_{carbido}$ bond hovers around 2.8 for all the terminal carbides examined, suggesting in essence an M-C triple bond.

CONCLUSION

In conclusion, DFT calculations predict stable, pseudotetrahedral, d^4 terminal carbide complexes with tripodal tris(*N*-heterocyclic-carbene) supporting ligands. All the complexes examined exhibit sizable singlet-triplet gaps and very small or negative electron affinities. Some exhibit low ionization potentials on the order of 4.5 eV, indicating sensitivity to oxidation. On the other hand, unlike in diatomics such as RhB, the calculations do not support a quadruple bond description for the metal carbide moiety in any of the complexes studied.

COMPUTATIONAL METHODS

All structures were optimized in gas phase with the scalar-relativistic ZORA[34] Hamiltonian, the B3LYP*[35,36] exchange-correlation functional, Grimme's D3[37] dispersion corrections, and all-electron ZORA Slater-type TZ2P basis sets, all as implemented in the ADF program system.[38] The tightest practicable criteria were used for both SCF and geometry cycles as well as for frequency analyses; the latter established the optimized structures as true minima. NBO analyses were performed based on single-point OLYP[39,40]-D3 calculations on the B3LYP*-D3 optimized geometries. All energies, including IPs, EAs, and E_{S-T}'s, are adiabatic values, obtained via a ΔSCF method, i.e., as differences in total electronic energy between the two states of interest. In general, the neutral complexes were all found to conform to C_{3v} symmetry, but the ionized and triplet states conformed only to C_s, as a result of Jahn-Teller distortions. None of the species examined evinced unduly small HOMO-LUMO gaps (or singlet-triplet gaps) so no compelling need was apparent for the deployment of multiconfigurational methods.

ASSOCIATED CONTENT
Supporting Information Available. Optimized DFT coordinates (9 pages).

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**Notes:** The authors declare no competing financial interests.

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TOC graphic

d_{z^2}-2s d_{z^2}-$2p_z$

Os(trisNHCmethane)(C)
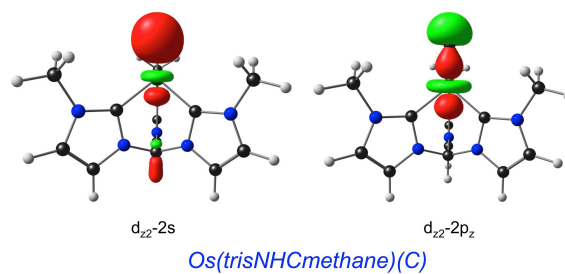
Synopsis. Scalar-relativistic DFT calculations predict a series of pseudotetrahedral Group 8 (Fe, Ru, Os) and Group 9 (Co, Rh, Ir) transition-metal terminal-carbide complexes with tris(N-heterocyclic-carbene) supporting ligands, with the metal-carbido interaction best described as a triple bond.