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A Ferracarborane Analogue to $[\text{Fp}]^-$. Synthesis and Reactions of
 $[\text{closo-3,3-(CO)}_2\text{-3,1,2-FeC}_2\text{B}_9\text{H}_{11}]^{2-}$

by

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Reduction of $[closo-3,3,3-(CO)_3-3,1,2-FeC_2B_9H_{11}]$ (1) with 2 equiv of sodium naphthalide affords the high-yield synthesis of a formal iron(0) ferracarborane dianion $[closo-3,3-(CO)_2-3,1,2-FeC_2B_9H_{11}]^{2-}$ (3), as monitored by ^{11}B NMR spectroscopy. Complex 3 serves as a nucleophile in a variety of alkylation, acylation, and metalation reactions to yield ferracarborane anions of the type $[closo-3,3-(CO)_x-3-L-3,1,2-FeC_2B_9H_{11}]^-$ (4, L = CH₃; 5, L = CH₂C₆H₅; 6, L = COCH₃; 7, L = SnC₆H₅). The molecular structure of $[N(C_2H_5)_4][7]$ has been determined by X-ray diffraction techniques. Compound 7 crystallized in the triclinic space group $P\bar{1}$ with $a = 11.209$ (1) Å, $b = 13.026$ (1) Å, $c = 13.595$ (1) Å, $\alpha = 79.959$ (3)°, $\beta = 84.143$ (3)°, $\gamma = 66.060$ (2)°, $V = 1785$ Å³, and $Z = 2$. In situ reactions of 3 with allyl and methylallyl chloride followed by subsequent loss of CO induced by ultraviolet radiation, resulted in the isolation of the corresponding η^3-allyl derivatives, $[closo-3-CO-3-(\eta^3-CH_2CH=CH_2)-3,1,2-FeC_2B_9H_{11}]^-$ (8, R = H; 9, R = CH₃). The structure of 8 as the PPN⁺ salt was also elucidated by single-crystal X-ray diffraction and found to crystallize in the monoclinic space group $P2_1/m$ with $a = 9.1250$ (7) Å, $b = 25.011$ (2) Å, $c = 18.517$ (2) Å, $\beta = 91.328$ (3)°, $V = 4225$ Å³, and $Z = 4$ (two crystallographically different half-anions and one cation in the asymmetric unit). Migratory				
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insertion of alkyls was demonstrated in the preparation of [*closo*-3-CO-3-COCH₃-3-P(CH₃)₃-3,1,2-FeC₂B₉H₁₁]⁻ (10) by heating 4 and excess P(CH₃)₃ in THF for 7 days at the reflux temperature. A single-crystal X-ray diffraction study of [PPN][10] is reported. Complex 10 crystallized in the triclinic space group *P* $\bar{1}$ with *a* = 10.086 (4) Å, *b* = 15.390 (6) Å, *c* = 17.027 (7) Å, α = 112.636 (8)°, β = 96.647 (8)°, γ = 100.206 (9)°, *V* = 2351 Å³, and *Z* = 2. The *closo* 12-vertex icosahedral geometry composed of a polyhedral FeC₂B₉-d₈ framework and pseudooctahedral coordination exhibited by the iron atom are common structural features displayed by all three of the ferracarboranes that were characterized crystallographically.

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