Carbenes

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# Dual Character of Arduengo Carbene–Radical Adducts: Addition versus Coordination Product[**]

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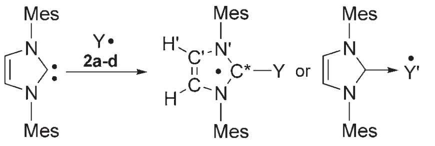
*Dedicated to Professor Herbert Mayr on the occasion of his 60th birthday*

Carbenes and radicals are among the most important reactive intermediates.[1] However, very little is known about their cross-reaction—the addition of a radical to a carbene to yield a new radical. This is mainly due to the generally short lifetime of these species which normally prevents the build up of sufficiently high concentrations of both species in the same reaction vessel. This situation has changed with the synthesis of stable carbenes **1**.[1b] Yet, except for a single study on the addition of a muonium to **1**,[2] very little is known on this fundamentally important reaction. To study such reactions the correct type of radicals has to be used. Radicals (Y$^\bullet$) need to be chosen so that in the adduct radicals the unpaired electron can interact with adjacent magnetically active atoms to provide useful EPR data. Thus, we chose the dialkoxyphosphoryl radical **2a** and the metal-centered radicals **2b**–**2d** as Y$^\bullet$ [Eq. (1)].



(1)

**1** **2a**: Y = P(O)(OPr-*i*)$_2$ **3a** Y' = [Y - CO]
**2b**: [Re(CO)$_5$] **3b**
**2c**: [Mn(CO)$_5$] **4c**
**2d**: [MoCp(CO)$_3$] **4d**
Mes = 2,4,6-trimethylphenyl Cp = $\eta^5$-cyclopentadienyl

Herein we report on the reactions of Arduengo carbene **1** with radicals Y$^\bullet$ and present the first EPR characterization of two types of novel paramagnetic products: a) the reaction of **1** with **2a** and **2b** yields the ring-centered radicals **3a** and **3b**, respectively; b) in the reaction with **2c** and **2d**, **1** substitutes a carbonyl ligand to yield novel, stable metal-centered radicals **4c** and **4d**, respectively, which correspond to carbene–metal coordination adducts [Eq. (1)]. This behavior contrasts with that of the heavier (silicon and germanium) congeners of **1**[3,4] that yield only ring-centered addition radical adducts. Characterization of the radical products **3a**,**b**, and **4c**,**d** by EPR spectroscopy and quantum-mechanical density functional theory (DFT) calculations allow important information to be obtained about their molecular and electronic structure, the spin distribution, as well as to gain a better understanding of the nature of the C–M bond in carbene–metal complexes.[5]

Irradiation ($\lambda > 300$ nm) of a benzene solution containing an equimolar concentration of **1** and [{(*i*PrO)$_2$(O)P}$_2$Hg] within the cavity of the EPR spectrometer yields an intense EPR spectrum consistent with radical **3a** (Figure 1). The main feature of the EPR spectrum of **3a** ($g = 2.0027$) is a doublet of quintets arising from hyperfine coupling (hfc) of the unpaired electron with the $^{31}$P nuclei ($I = 1/2$; $a_P = 48.7$ G) and with two magnetically equivalent $^{14}$N nuclei ($I = 1$; $a_N = 4.7$ G; Figure 1a). The expanded line in the EPR spectrum of **3a** (Figure 1b) shows a poorly resolved triplet arising from hfc between the unpaired electron and the two equivalent protons (H, H′) of the heterocycle ($a_H = 1.1$ G). This hfc

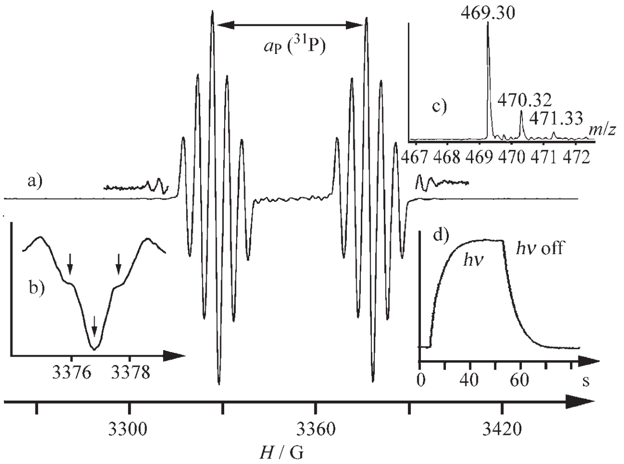


**Figure 1.** a) EPR spectrum of a solution of **3a** in benzene recorded at 298 K under UV irradiation; b) second derivative of the expanded line; c) mass spectrum (MALDI-TOF) of **3a**; d) kinetic curve of the generation and decay of radical **3a**.

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constant is significantly smaller than in various radical adducts of the analogous silylene adduct **2**[3a] and germylene adduct **3**[3b,c] ($a_H = 4.7$–$6.0$ G). This result indicates a lower spin density on the two heterocyclic carbon atoms in **3a** than in the analogous higher congeners. Thus, the spin density in **3a** is more localized on the central carbon (C*) atom than in the analogous silicon[3a] and germanium[3b,c] species. At high gain, the spectrum of **3a** shows additional satellite lines arising from hyperfine interaction of the unpaired electron with the central $^{13}C^*$ ($I = 1/2$) nuclei ($a_C = 25.6$ G). MALDI-TOF MS analysis of the reaction mixture shows signals corresponding to the molecular weight of **3a** (Figure 1c).[6] When the UV irradiation is turned off, a fast decay of the EPR signal of **3a** is observed ($\tau_{1/2} = 7.1$ s; Figure 1d).

Addition to **1** of $[(CO)_5Re^\bullet]$ (**5b**), generated by UV irradiation ($\lambda > 300$ nm) of a solution of $[Re_2(CO)_{10}]$ in benzene, yields radical adduct **3b** (g = 2.004). In contrast to the short-lived **3a** ($\tau_{1/2} = 7.1$ s), **3b** is persistent at room temperature for several days ($\tau_{1/2} = 2$ days).[7] The EPR spectrum of **3b** shows hfc with two equivalent $^{14}N$ atoms ($a_N = 7.1$ G), with two protons ($a_H = 4.73$ G), and with the $^{185,187}Re$ nucleus ($I = 5/2$; $a_{Re} = 41.1$ G; Figure 2a). These hfc constants are very similar to the hfc constants observed on addition of Re-centered radicals to silylene **2**[3a] and germylene **3**.[3b] This similarity and the higher $a_H$ value in **3b** compared to **3a** can be explained by a higher contribution of resonance structure **3b′** [Eq. (2)].[8] The formation of **3b** is supported by MALDI-TOF mass spectroscopy, which shows signals corresponding to **3b** (Figure 2c).

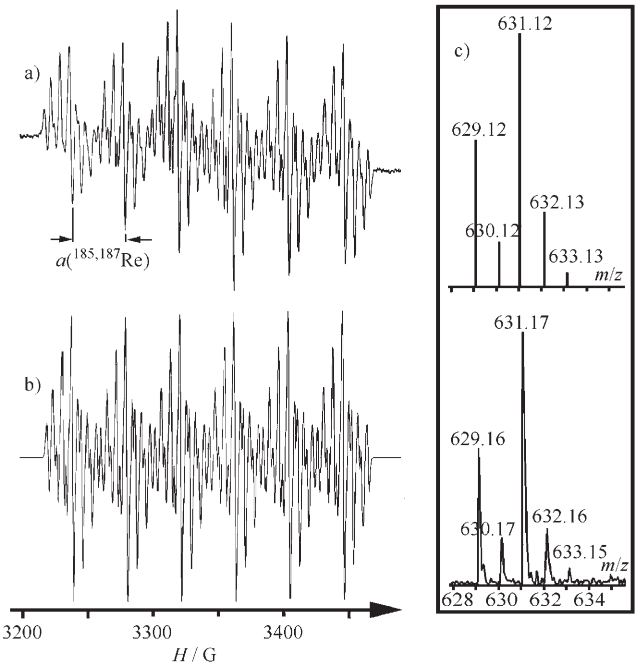
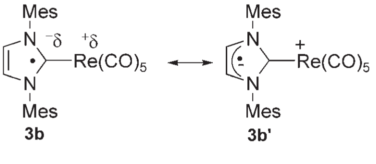


**Figure 2.** a) Experimental and b) simulated EPR spectra of **3b** at 298 K; c) experimental (bottom) and simulated (top) mass spectrum (MALDI-TOF) of **3b**.



(2)

Reaction of **1** with $[(CO)_5Mn^\bullet]$ leads to a different type of product, as evident from the unusual EPR spectrum of **4c** (Figure 3) showing hyperfine coupling only with the $^{55}Mn$ nucleus ($I = 5/2$; $a_{Mn} = 24.0$ G) and a significantly downfield shifted g-factor of 2.023 (g = 2.004 for **3b**). This result suggests that the product is a Mn-centered radical in which one of the carbonyl ligands has been substituted by carbene **1**, and we assign to it structure **4c**. Radical **4c** is relatively stable at room temperature ($\tau_{1/2} = 16$ h).[9] The difference in the reaction course between **1** and $[(CO)_5Re^\bullet]$ (which yields a metal-substituted radical **3b**), and its reaction with $[(CO)_5Mn^\bullet]$ (which produces a metal-centered complex **4c**), may result from the known two orders of magnitude faster substitution of CO in Mn carbonyl complexes than in analogous Re carbonyl complexes.[10]

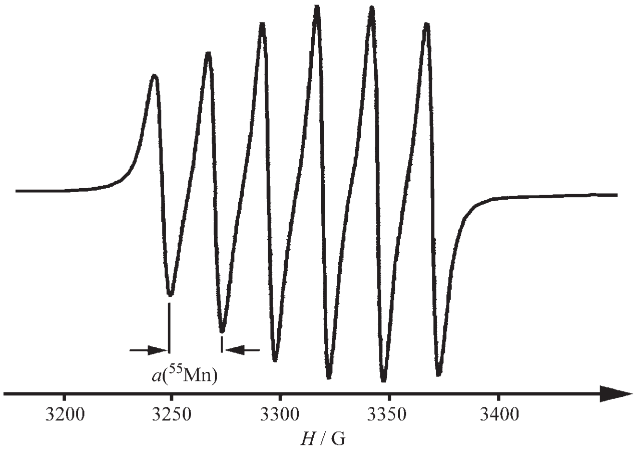


**Figure 3.** EPR spectra of **4c** at 330 K.

Substitution of a carbonyl ligand and the generation of a metal-centred radical also occurs in the reaction of **1** with $[(CO)_3CpMo^\bullet]$ to yield adduct **4d** ($\tau_{1/2} = 12$ h). The EPR spectrum of paramagnetic **4d**, similar to **4c**, is characterized by hyperfine interaction only with the $^{95,97}Mo$ atom (natural abundance 25.5 %, $I = 5/2$; $a_{Mo} = 16.7$ G at 260 K) and by a downfield shifted g-factor (g = 2.061). The EPR signal of **4d** in frozen toluene glass shows strong anisotropy of the g-factor, which results in three EPR signals ($g_1 = 2.129$, $g_2 = 2.061$, $g_3 = 1.993$) typical for metal-centered radicals. Similar high anisotropic g-factor values were observed for the isoelectronic chromium-centered radical $[Cp(CO)_3Cr^\bullet]$ ($g_1 = 2.134$, $g_2 = 2.035$, $g_3 = 1.997$).[11]

DFT calculations[12] were carried out to provide information on the molecular and electronic structures as well as the spin-density distributions in radicals **3a** (UB3LYP/6-311+G-(2d,p)//UB3LYP/6-31G(d)) and **4c** (UB3LYP/TZVP//

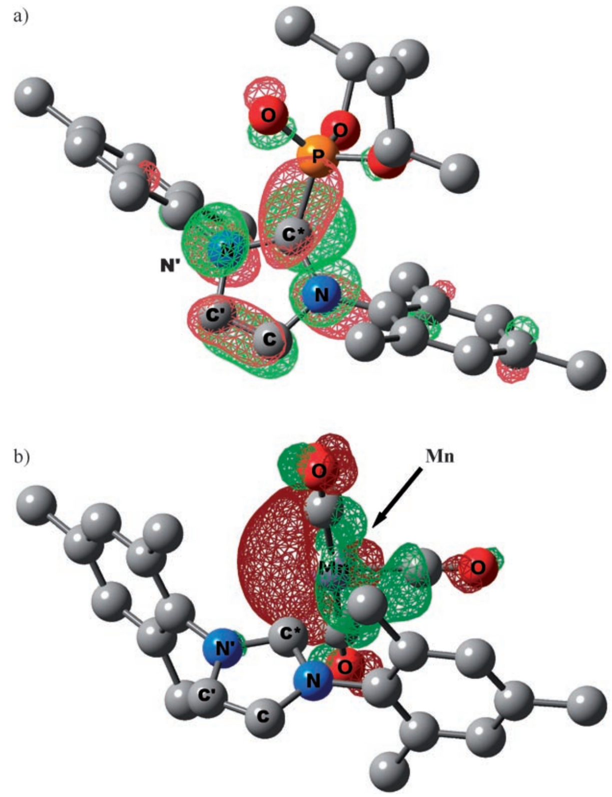


*Figure 4.* Calculated SOMOs, absolute values of hfc constants, Mulliken atomic spin densities (in parentless), and selected bond lengths [Å] and angles [°] of a) radical **3a**: $a(^{13}\mathrm{C}^*) = 19.1$ G (53.3 %), $a(^{31}\mathrm{P}) = 41.4$ G (4.6 %), $a(^{14}\mathrm{N}) = 2.3$ G (12.6 %), $a(^{14}\mathrm{N}') = 2.5$ G (17.1 %), $a(^{13}\mathrm{C}) = 0.6$ G (3.3 %), $a(^{13}\mathrm{C}') = 1.8$ G (1.9 %), $a(^{1}\mathrm{H}) = 1.1$ G (0.39 %), $a(^{1}\mathrm{H}') = 0.5$ G (0.16 %); C*-N 1.422, C*-N′ 1.420, N-C 1.400, N′-C′ 1.390, C-C′ 1.349, C*-P 1.781, $\Sigma\theta$(N) 359.23, $\Sigma\theta$(C*) 352.34, $\Sigma\theta$(N′) 359.19, C*-N-C-C′ 0.51, C*-N′-C′-C −0.46; b) radical **4c**: $a(^{13}\mathrm{C}^*) = 8.7$ G (0.97 %), $a(^{31}\mathrm{Mn}) = 40.3$ G (84.6 %), $a(^{14}\mathrm{N}) = 0.55$ G (0.12 %), $a(^{14}\mathrm{N}') = 2.3$ G (0.67 %), $a(^{13}\mathrm{C}) = 0.34$ G (0.12 %), $a(^{13}\mathrm{C}') = 0.004$ G (0.11 %), $a(^{1}\mathrm{H}) = 0.14$ G (0.01 %), $a(^{1}\mathrm{H}') = 0.40$ G (0.04 %); C*-N 1.369, C*-N′ 1.371, N-C 1.393, N′-C′ 1.393, C-C′ 1.352, C*-Mn 2.083, $\Sigma\theta$(N) 360.00, $\Sigma\theta$(C*) 360.00, $\Sigma\theta$(N′) 360.00, C*-N-C-C′ 0.01, C*-N′-C′-C 0.06.

UB3LYP/6-31+G(df)).[13] The calculated molecular structures and the singly occupied molecular orbitals (SOMO) of **3a** and **4c** are shown in Figure 4a and b, respectively. The central carbon atom in **3c** is slightly pyramidal ($\Sigma\Theta(\mathrm{C}^*) = 352.3°$), which is in contrast to that in **4c**, which is completely planar ($\Sigma\Theta(\mathrm{C}^*) = 360.0°$). The heterocycle is essentially planar in both **3a** and **4c** (∡C*-N-C-C′ = 0.51° and ∡C*-N′-C′-C = −0.46° in **3a**; ∡C*-N-C-C′ = 0.01° and ∡C*-N′-C′-C = 0.06° in **4c**). The calculated Mulliken spin density of **3a** indicates that 53 % of the spin density is localized on the central carbon atom (C*) and 34 % on the other ring atoms. In contrast, 85 % of the spin density is localized on the manganese atom in **4c**. These values are consistent with the shape of the SOMO (Figure 4), and they are in good agreement with the experimental EPR data of **3a** and **4c** (discussed above).

The addition reaction of a methyl radical to **1** is moderately exothermic (−16.0 kcal mol$^{-1}$ at UB3LYP/6-31+G(d,p)//UB3LYP/6-31+G(d,p)).[12,14] The addition of a methyl radical to $(\mathrm{CH_3})_2\mathrm{C}$: (singlet) is much more exothermic (−83.0 kcal mol$^{-1}$), as expected from the higher stability of **1**. This result indicates that addition of free alkyl radicals to a wide variety of carbenes is expected to be exothermic and thus has a high potential to yield new radicals.

In summary, we have demonstrated for the first time that Arduengo carbene **1** can undergo radical addition to produce two novel groups of radicals, either ring-centered radicals or carbene-coordinated metal-centered radicals, and report their EPR spectra which provide insights into their electronic structure and spin distribution. There are major stability differences between the radical adducts of a phosphoryl radical and the metal-centered radicals, the latter being significantly more stable. We are continuing to explore this interesting new class of radical reactions.

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[6] The observation in the MALDI-TOF mass spectrum of signals corresponding to radical **3a** may result from the dissociation of the corresponding dimer or from the reaction between reactants left in the crude mixture.

[7] The higher stability of **3b** compared with **3a** can be explained by the higher polarity of the C−Re bond compared with a C−P bond, making dimerization of **3b** less favorable compared to dimerization of **3a**.

[8] Similar spin-density distribution was reported for an anion radical of an N-heterocyclic carbene ($a_{\mathrm{H}}(2\mathrm{H}) = 3.27$ G; $a_{\mathrm{N}}(2^{14}\mathrm{N}) = 6.02$ G), see P. L. Arnold, S. T. Liddle, *Chem. Commun.* **2006**, 3959.

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