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Indirect "through-space" $^{13}C–^{31}P$ coupling in isostructural nickel, palladium, and platinum complexes: spin transmission mediated by sulfur atoms

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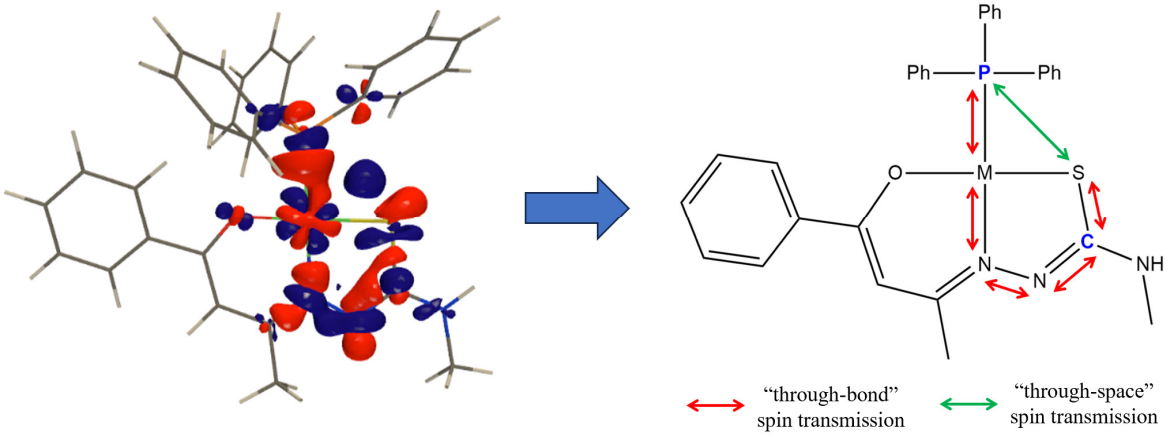
Indirect "through-space" spin-spin coupling has been identified in many organic molecules since the late 1950s, and to a lesser extent, it has also been reported in coordination compounds[1]. In this work, we present the synthesis and characterization of the isostructural square-planar complexes $[Ni^{II}(bmt)PPh_3]$ (**1**), $[Pd^{II}(bmt)PPh_3]$ (**2**), and $[Pt^{II}(bmt)PPh_3]$ (**3**), where bmt = 5-hydroxy-*N*,3-dimethyl-5-phenyl-4,5-dihydro-1*H*-pyrazole-1-carbothioamide dianion. The complexes were characterized by elemental analysis, FTIR spectroscopy, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, mass spectrometry, and single crystal X-ray diffraction. In all complexes, an unusual $^{13}C–^{31}P$ coupling has been observed: $^3J_{C–P}$ of a thiocarbonyl carbon is exceedingly larger than the other observed $^3J_{C–P}$. Theoretical investigation has been employed to give a better understanding of the nature of this coupling, which was found to be dominated by intricate interplays of unusual "through-space" and "through-bond" coupling mechanisms (Figure 1). The results indicated that the "through-space" component is dominated by an interaction between σ(M–P) and σ*(S–C) orbitals, a finding that offers new insights into indirect spin-spin coupling in coordination compounds. The literature only reports "through-space" couplings where at least one electron lone pair is directly involved[1,2]. In our case, the "through-space" component of the $^{13}C–^{31}P$ coupling pathway has no significant lone pair role, advancing our understanding of how such couplings operate.

Figure 1. Coupling deformation density (CDD) of $^3J_{C–P}$ in the thiocarbonyl carbon of complex **1** (left) and a schematic illustration of the coupling pathways (right). Isosurface value of 0.02 a.u.



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