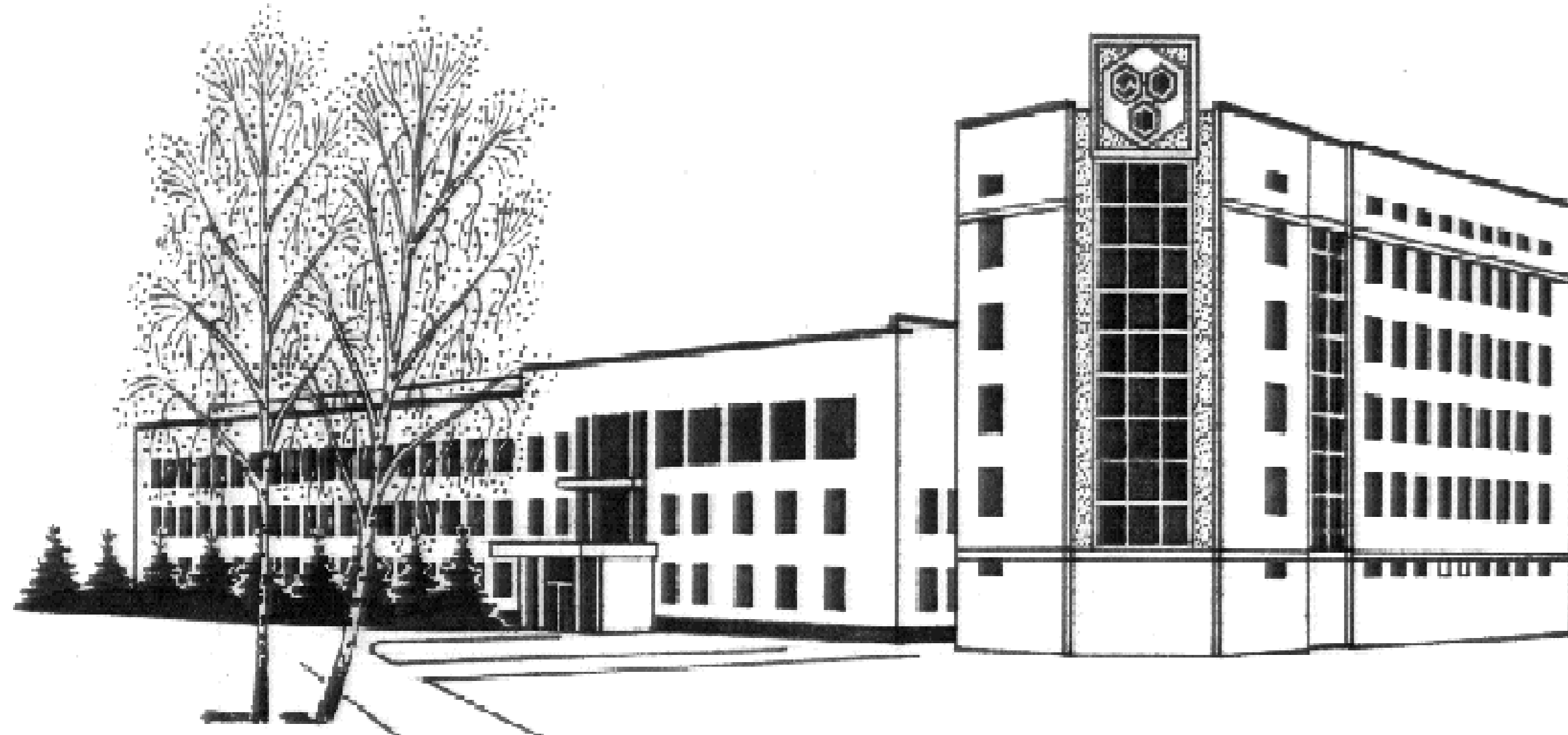


SYNTHESIS, STRUCTURE AND REACTIVITY OF ORGANOGOLD NITRONYL NITROXIDE DERIVATIVES STABILIZED BY PHOSPHINE LIGANDS



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Introduction

Organogold nitronyl nitroxide derivatives with a phosphine ligands (NN-Au-PR₃), are interesting type of paramagnetic compounds in terms of their unique structure and electronic and electrochemical properties [1]. The advantage of these organogold compounds is that they have high stability in solid and dissolved states in contrast to the NN-2-ide radical anion ($\tau < 30$ min at room temperature [2]). Moreover, a triphenylphosphine gold derivative of an NN called NN-Au-PPh₃ is known to enter into a Pd(0)-catalyzed cross-coupling reaction with aryl iodides and bromides, with the former reacting smoothly in most cases and the latter being less active and interacting only in the presence of electron acceptor substituents [1]. On the other hand, there are no reports on how variation of the phosphine ligand influences the Pd(0)-mediated cross-coupling process.

Therefore, **the main concept of the work** is to study how substituting phosphine ligands would impact the reactivity of NN-Au-PR₃ in Pd(0) cross-coupling reaction.

Results

We started our investigation with performing the synthesis of two new paramagnetic derivatives, NN-Au-P^tBuPh₂ (**1**) and NN-Au-P^tBu₂Ph (**2**), containing one and two bulky tert-butyl substituents, respectively (Figure 1).

The compounds obtained were characterized by X-ray diffraction analysis, cyclic voltammetry, and ESR, IR, and UV/Vis spectroscopy [3].

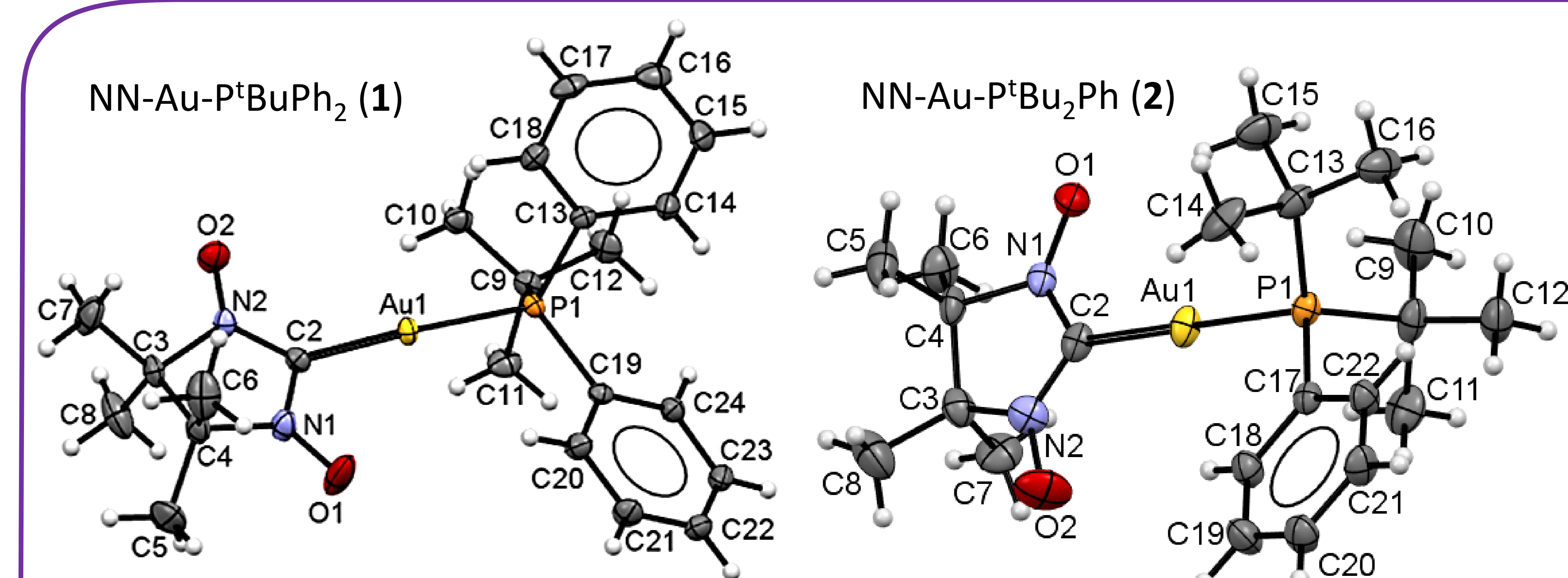


Figure 1. The molecular structures of NN-Au-P^tBuPh₂ (**1**) and NN-Au-P^tBu₂Ph (**2**).

XRD analysis revealed that the derivatives synthesized formed the unusually large number (5-6) of short intermolecular contacts involving nitonyl nitroxide fragment, which was owing to the anionic character of the paramagnet group. The latter confirms the low oxidative potential of NN-Au-PR₃ (~ -0.05 V) in comparison with NN-H (+0.38 V).

According to ESR spectroscopy the compounds **1** and **2** have similar spectra with the parameters $A(2N) = 0.795$ mT, $A(P) = 0.225$ mT, $g_{iso} = 2.0071$ (**1**); $A(2N) = 0.800$ mT, $A(P) = 0.215$ mT, $g_{iso} = 2.0068$ (**2**), which is close to NN-Au-PPh₃ [1] (Figure 2).

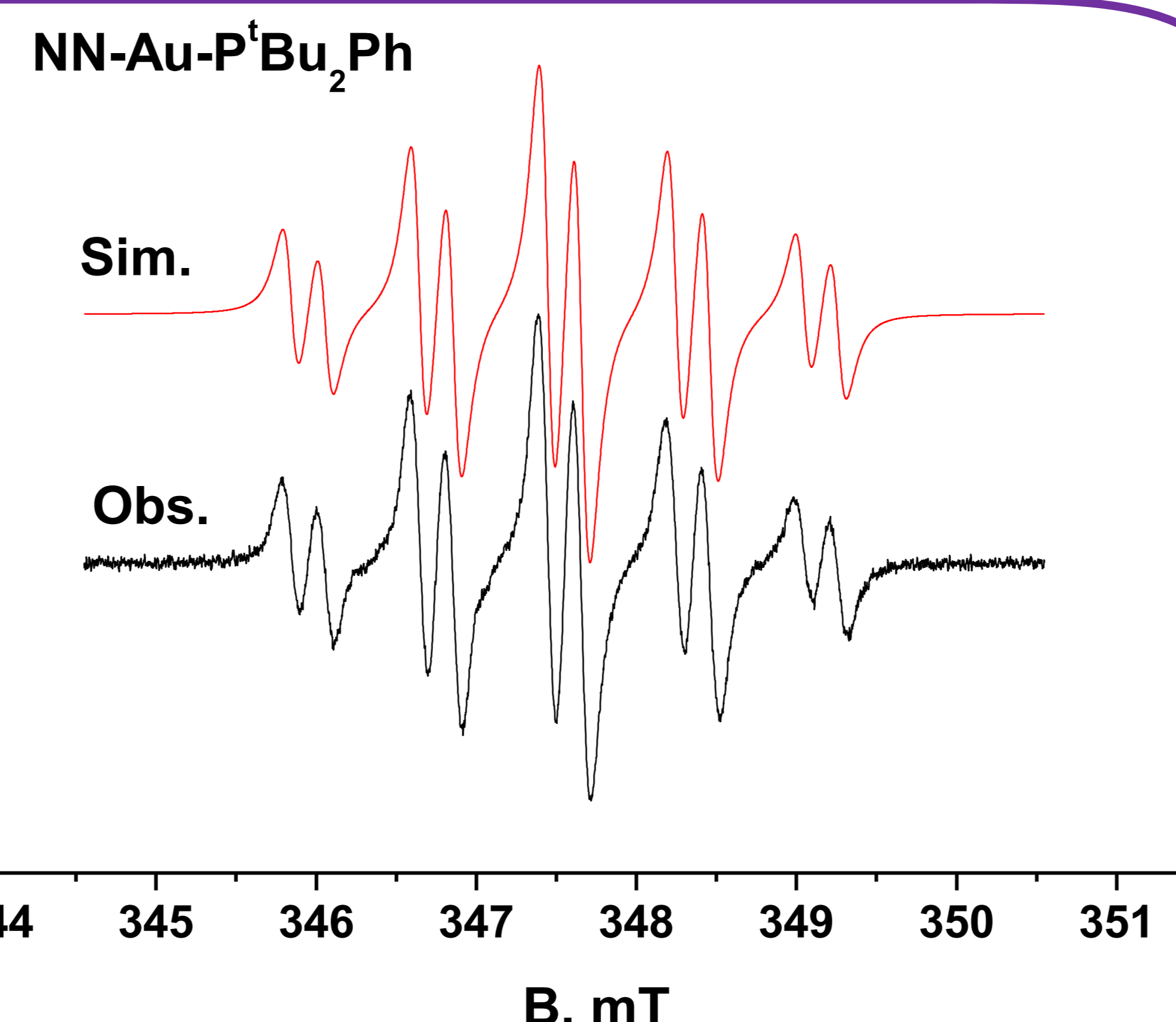
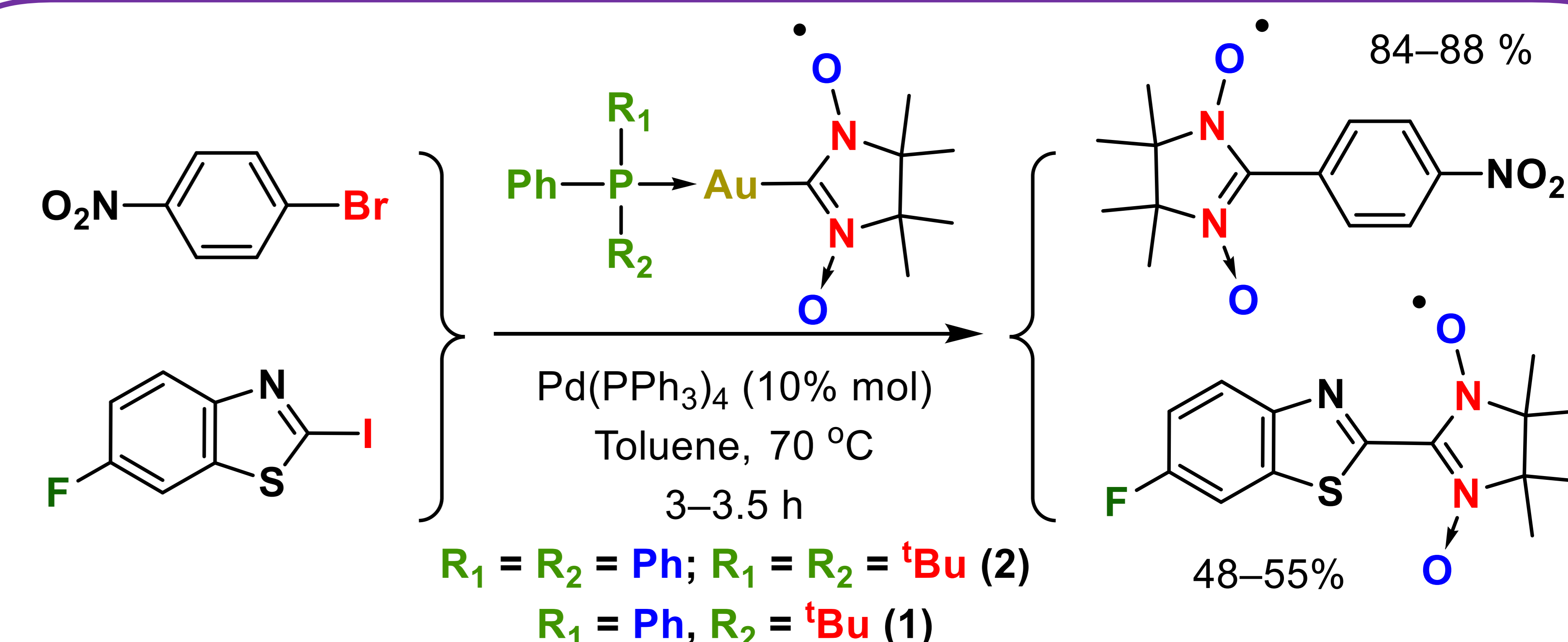


Figure 2. The ESR spectrum for a toluene solution of NN-Au-P^tBu₂Ph (**2**).



To investigate the relation between the structure of the gold complexes and their reactivity, we carried out the Pd(PPh₃)₄-catalyzed cross-coupling reaction of NN-Au-PPh₃, NN-Au-P^tBuPh₂ (**1**) and NN-Au-P^tBu₂Ph (**2**) with p-bromonitrobenzene and 6-fluoro-2-iodobenzothiazole. The experiments showed that there were no considerable differences between reactivity of these organogold derivatives in the cross-coupling process under selected conditions. **Thus, the bulky tert-butyl phosphine ligand practically do not affect both the reaction rate and the the product yield.**

[1] Tanimoto R., Suzuki S., Kozaki M., Okada K. // Chem. Lett. 2014. Vol. 43. P. 678–680.

[2] Suzuki S., Kira S., Kozaki M., Yamamura M., Hasegawa T., Nabeshima T., Okada K. // Dalton Trans. 2017. Vol. 46. P. 2653–2659.

[3] Zayakin, I., Bagryanskaya I., Stass D., Kazantsev M., Tretyakov E. // Crystals 2020, Vol. 10. P. 770.4