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Synthesis and Structure of (Nitronyl Nitroxide-2-ido)(*tert*-butyldiphenylphosphine)gold(I) and -(Di(*tert*-butyl)phenylphosphine)gold(I) Derivatives; Their Comparative Study in the Cross-Coupling Reaction

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Abstract: We synthesized two new organogold derivatives of a nitronyl nitroxide (NN) with phosphine ligands, namely NN-Au-P^tBuPh₂ and NN-Au-P^tBu₂Ph. They were characterized by X-ray diffraction analysis, cyclic voltammetry, and ESR, IR, and UV/Vis spectroscopy. The X-ray structural analysis revealed a tendency of the NN moiety to form a large number of short intermolecular contacts. This phenomenon is related to the anionic nature of the paramagnetic group NN, as evidenced by a significantly lower oxidation potential in comparison with purely organic derivatives of NN radicals. The cross-coupling reaction of NN-Au-PPh₃, NN-Au-P^tBuPh₂, or NN-Au-P^tBu₂Ph with an activated bromoarene, namely, *p*-BrC₆H₄NO₂, was investigated. It was shown that regardless of the presence of the bulky *tert*-butyl substituent, all gold derivatives have similar activities in the cross-coupling reaction and give a cross-coupling product, NN-C₆H₄NO₂, with comparable yields.

Keywords: nitronyl nitroxide; organogold derivatives; X-ray diffraction analysis; ESR spectroscopy; Pd(0)-catalyzed cross-coupling

1. Introduction

(Nitronyl nitroxide-2-ido)-Au, i.e., (NN-2-ido)-Au, organometallic derivatives with a phosphine ligand developed by K. Okada et al., are interesting types of paramagnetic compounds in terms of their unique structure and electronic and electrochemical properties [1] (Figure 1). The advantage of these organogold derivatives 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]). Therefore, these metal–radical species are expected to be applicable to various fields of science.

Figure 1. Previously reported NN-Au-phosphine organometallic derivatives.

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. One would expect two types of such an influence: via electronic effects and via steric effects. Here, we concentrated on the latter by performing the synthesis of two paramagnetic derivatives, NN-Au-P^{*t*}BuPh₂ (1) and NN-Au-P^{*t*}Bu₂Ph (2) (Figure 2), containing one and two bulky *tert*-butyl substituents, respectively. Both paramagnetic compounds were completely characterized (including X-ray diffraction [XRD] analysis) and then were studied together with a structurally related compound, NN-Au-PPh₃, in a cross-coupling reaction with an activated bromoarene, namely *p*-BrC₆H₄NO₂.

Figure 2. Newly synthesized NN-Au-P^{*t*}BuPh₂ (1) and NN-Au-P^{*t*}Bu₂Ph (2).

2. Materials and Methods

2.1. General Procedures

4,4,5,5-Tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl [3] and (NN-2-ide) (triphenylphosphine)gold [4] were synthesized as reported earlier. Other chemicals were of the highest purity commercially available and were used as received. All the solvents were of reagent quality. The reactions were monitored by thin-layer chromatography on silica gel 60 F₂₅₄ aluminum sheets from Merck. The chromatography was carried out using silica gel (0.050–0.160 mm) for column chromatography. Infrared (IR) spectra were obtained from KBr pellets by means of a Bruker VECTOR 22 infrared spectrometer. Continuous-wave ESR spectra were acquired on a Bruker ER200D X-band spectrometer at MW power 2 mW with modulation 0.01 mT/100 kHz. Cyclic voltammetry measurements were performed in a CH₂Cl₂ solution with a computer-controlled P-8nano potentiostat/galvanostat (Elins, Russia) in combination with a three-electrode cell (Gamry, Warminster, PA, USA); 0.1 M tetrabutylammonium hexafluorophosphate was used as a supporting electrolyte. Pt, a Pt wire, and Ag/AgCl served as working, counter, and reference electrodes, respectively. The cell was calibrated by measurement of the redox potential of ferrocene as an internal standard.

2.2. Synthetic Procedures

2.2.1. Chloro(*tert*-butyldiphenylphosphine)gold

Chloroauric acid trihydrate (0.1 g, 0.254 mmol) was dissolved in EtOH (2 mL) under argon followed by the addition of phosphine (0.123 g, 0.508 mmol). The reaction mixture was stirred for 24 h at room temperature. A white precipitate formed, and the solution became colorless. The resulting mixture was evaporated under reduced pressure, and the residue was recrystallized from CH₂Cl₂–hexane (1:1) to prepare the title product with yield 0.080 g (67%). The spectral characteristics were identical to those reported before [5].

2.2.2. Chloro(di(*tert*-butyl)phenylphosphine)gold

This compound was prepared similarly to chloro(*tert*-butyldiphenylphosphine)gold with yield 65%. The spectral characteristics were identical to those presented in ref. [6].

2.2.3. (4,4,5,5-Tetramethyl-3-oxide-1-oxyl-4,5-dihydro-1*H*-imidazol-2-yl)(*tert*-butyldiphenylphosphine)gold (1)

To a solution containing ^tBuPh₂PAuCl (0.1 g, 0.211 mmol) and 4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (NN-H) (0.033 g, 0.211 mmol) in CH₂Cl₂ (1.5 mL), a 0.64 M NaOH solution in MeOH (0.330 mL, 0.211 mmol) was added. The reaction mixture was stirred for 2 h. The solvent was removed by evaporation under reduced pressure. To the residue, CH₂Cl₂ was added, the mixture was passed through a glass filter, and the filtrate was concentrated. The residue was crystallized from a CH₂Cl₂–Et₂O–heptane mixture at −5 °C. Yield 0.120 g, (96%); blue-purple crystals; IR (KBr, cm^{−1}): 457 w, 501 m, 528 m, 538 m, 604 w, 621 w, 634 vw, 698 s, 725 s, 758 m, 808 vw, 841 w, 935 vw, 999 w, 1014 w, 1028 vw, 1076 w, 1099 m, 1138 m, 1155 m, 1178 m, 1211 m, 1273 m, 1327 vs, 1365 m, 1381 w, 1392 w, 1437 m, 1464 m, 1479 m, 1587 vw, 1633 w, 2866 w, 2929 w, 2970 m, 2985 m, 3039 m, 3068 vw, 3089 vw, 3442 m; UV/Vis (CH₂Cl₂): λ_{max} (ε) = 367 (13,392), 563 nm (1416 M^{−1}·cm^{−1}).

2.2.4. (4,4,5,5-Tetramethyl-3-oxide-1-oxyl-4,5-dihydro-1*H*-imidazol-2-yl)(di(*tert*-butyl)phenylphosphine)gold (2)

This substance was synthesized by a technique analogous to the one described above. Yield 0.095 g, (88%); blue-purple crystals; IR (KBr, cm^{−1}): 457 vw, 480 w, 495 w, 522 m, 538 w, 594 w, 621 w, 702 m, 750 m, 760 w, 810 w, 839 w, 939 vw, 999 w, 1024 w, 1101 m, 1138 m, 1153 m, 1178 m, 1213 m, 1315 s, 1331 vs, 1367 m, 1383 w, 1390 m, 1435 m, 1464 m, 1475 m, 1535 w, 1585 vw, 1632 w, 1639 w, 1659 w, 1693 w, 2866 w, 2901 w, 2958 m, 2980 m, 2999 w, 3032 vw, 3059 w, 3091 vw, 3437 m; UV/Vis (CH₂Cl₂): λ_{max} (ε) = 364 (14,653), 561 nm (1436 M^{−1}·cm^{−1}).

2.2.5. The General Protocol for the Palladium-Catalyzed Cross-Coupling Reactions

An aryl halide (1.0 eq.), an Au complex (1.0 eq.), and Pd(PPh₃)₄ (10 mol%) were dissolved in toluene under argon. The mixture was heated at 70 °C until total consumption of the Au complex. Next, the solvent was removed by rotary evaporation. The residue was purified by column chromatography (SiO₂, CH₂Cl₂–hexane [2:1] as the eluent) to obtain 2-(4-nitrophenyl)NN. Analytical characteristics of the product were identical to those published earlier [4].

2.3. Single-Crystal XRD Analysis

X-ray crystallographic analysis of the crystals was carried out at 296(2) K on a Bruker Kappa Apex II CCD diffractometer using φ, ω -scans of narrow (0.5°) frames with Mo K α radiation (λ = 0.71073 Å) and a graphite monochromator. The structures were solved by direct methods using the SHELX-97 software [7] and refined by the full-matrix least-squares method against all F² in anisotropic approximation in the SHELXL-2014/7 software [8]. Absorption corrections were applied via the empirical multiscan method in the SADABS 2008/1 software [9]. The hydrogen atoms' positions

were calculated with the riding model. Solvating molecules of CH_2Cl_2 were observed in the crystal packing of **1**. Crystals of **2** contain two crystallographically independent molecules. Crystal data and structure refinement details are listed in Table 1.

Table 1. XRD data for compounds **1** and **2**.

Compound	1	2
Empirical formula	$\text{C}_{23}\text{H}_{31}\text{AuN}_2\text{O}_2\text{P}\cdot\text{CH}_2\text{Cl}_2$	$\text{C}_{21}\text{H}_{35}\text{AuN}_2\text{O}_2\text{P}$
Formula weight	680.36	575.44
Crystal system	Orthorhombic	Triclinic
Space group	$\text{P}2_12_12$	$\text{P}-1$
Unit cell dimensions: a , Å	12.4455(3)	11.6327(5)
b , Å	18.8187(4)	13.9580(7)
c , Å	11.3588(3)	15.1761(7)
α, β, γ , °	90, 90, 90	78.038(2), 88.912(2), 78.333(2)
Volume, Å ³	2660.3(1)	2360.14(19)
Z	4	4
Density (calcd.), $\text{mg}\cdot\text{m}^{-3}$	1.699	1.619
Abs. coefficient, mm^{-1}	5.814	6.318
$F(000)$	1340	1140
Crystal size, mm^3	$0.20 \times 0.40 \times 0.55$	$0.02 \times 0.20 \times 0.30$
Θ range, °	2.4–30.7	2.6–26.0
Index ranges	$-17 \leq h \leq 17, -25 \leq k \leq 26,$ $-16 \leq l \leq 16$	$-15 \leq h \leq 15, -18 \leq k \leq 18,$ $-19 \leq l \leq 20$
Reflections collected	38,693	50,204
Independent reflections	7279 $R(\text{int}) = 0.049$	12,227 $R(\text{int}) = 0.058$
Completeness to θ , %	99.6 ($\theta \leq 50^\circ$)	99.8 ($\theta \leq 50^\circ$)
Data/restraints/parameters	7279/0/295	12,227/0/506
Goodness-of-fit on F^2	1.06	1.04
Final R indices $I > 2\sigma(I)$	$R_1 = 0.0252, wR_2 = 0.0571$	$R_1 = 0.0424, wR_2 = 0.0903$
Final R indices (all data)	$R_1 = 0.0300, wR_2 = 0.0593$	$R_1 = 0.0711, wR_2 = 0.0992$
Largest diff. peak/hole, $\text{e}\cdot\text{\AA}^{-3}$	0.72/−0.86	1.69/−1.32

CCDC 2019815 and 2019816 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

3. Results and Discussion

3.1. Syntheses and Structures of $\text{NN-Au-P}^t\text{BuPh}_2$ and $\text{NN-Au-P}^t\text{Bu}_2\text{Ph}$ in Comparison with NN-Au-PPh_3

Metalloid radicals $\text{NN-Au-P}^t\text{BuPh}_2$ (**1**) and $\text{NN-Au-P}^t\text{Bu}_2\text{Ph}$ (**2**) were successfully prepared by the addition of NaOH/MeOH to a CH_2Cl_2 solution containing NN-H and corresponding $\text{Cl-Au-P}^t\text{BuPhR}$ (1:1 ratio) in a 96% (**1**) and 88% (**2**) yield. Radicals **1** and **2** were stable under aerated conditions and were studied both in solution and in a solid state. Bluish-purple single crystals of **1** and **2** used in the structure determination were grown by slow evaporation of CH_2Cl_2 – Et_2O –heptane solutions at -5°C .

The X-ray crystallographic analyses revealed that **1** crystallizes in orthorhombic space groups $\text{P}2_12_12$, whereas **2** crystallizes in the triclinic $\text{P}-1$ space group. ORTEP diagrams of compounds **1** and **2** (one of two independent molecules) drawn with 50% ellipsoid probability are depicted in Figure 3. In the synthesized organogold derivatives, bond lengths $\text{Au}-\text{C}2$ [2.034(4) for **1**; 2.043(6) and 2.039(5) Å for **2**] and NO [1.292(5) and 1.285(6) Å for **1**; 1.302(6) and 1.276(8) as well as 1.286(6) and 1.282(6) Å for **2**] are close to those of previously described NN-Au-PPh_3 ($\text{Au}-\text{C}2$: 2.032 Å, NO : 1.286 and 1.287 Å) [4]. The dihedral angles between $\text{N}1=\text{C}2-\text{N}2$ and $\text{C}3-\text{C}4$ moieties are 21.6° for **1**; as for the two independent structures of compound **2**, they have similar absolute angle values but differ in the sign

(-21.9° and 23.6°). The C–Au–P bond angles for NN–Au–PPh₃, **1**, and **2** are in the range 177 – 179° , in good agreement with those in analogous organogold(I) phosphanes [10–12].

Figure 3. ORTEP view and the atom numbering scheme of NN–Au–P^tBuPh₂ (**1**) and NN–Au–P^tBu₂Ph (**2**, one of two independent molecules) with displacement ellipsoids at a 50% probability level.

The crystal structures were analyzed for short contacts between nonbonded atoms using software packages PLATON-2003 [13,14] and MERCURY-2020.1 (Build 280197) [15]. The analysis revealed that the crystal packing in NN–Au–PPh₃, **1**, and **2** is secured by intermolecular short contacts predominantly with the participation of the atoms of the NN moiety. Moreover, the number of such contacts is unusually large and reaches five in the gold derivative NN–Au–PPh₃ (Table 2). For comparison, in purely organic NNs, the paramagnetic moiety participates in the formation of a limited number of short contacts, one or two, very rarely three contacts. The tendency of radicals NN–Au–PPh₃, **1**, and **2** to form an increased number of short contacts in the solid state is due to the anionic nature of the NN part, which effectively attracts positively charged atoms of neighboring molecules. This situation leads to supramolecular assembly of the gold derivatives into complicated 3D structures. To simplify their analysis, it is reasonable to choose lower-dimensional substructures and then to connect them via the short contacts to build the final 3D structures of paramagnets.

In NN–Au–PPh₃, as a suitable substructure, one can choose the centrosymmetric dimer in which the molecules are linked by van der Waals interactions of type C_{Ph}–H...O2 (contacts *i*, Figure 4a) leading to short distances C_{Ph}–H ... N (*ii*) and C_{Ph}–H ... C (*iii*). The binding of molecules into dimers also causes the formation of short contacts *iv* between the carbon atoms of the aromatic rings. The propagation of the dimers via two intermolecular C_{Me}–H...O1 van der Waals interactions (contacts *v* and *vi*) and short contacts C–H...C *vii* generates infinite layers (Figure 4b). The layers are bonded to each other due to additional contacts C_{Ph}–H...O1 (*viii*) and C_{Ph}–H...O2 (*x*) formed with the participation of oxygen atoms of the paramagnetic centers (Figure 4c).

In the case of gold derivative **1**, the dimer shown in Figure 5a can serve as a suitable substructure. In the dimer, the molecules are linked by two van der Waals interactions C_{Ph}–H...O2 (contacts *i*, Figure 5a); the binding of molecules leads to short contacts between H atoms (contact *ii*). Next, the binding of the dimeric structures into the 3D framework occurs both through direct contacts of type C_{Ph}–H...O2 (*iii*) and via short contacts with bridging solvation molecules (Figure 5b).

Table 2. The parameters of short contacts and interatomic distances for NN-Au-PPh₃ [4], NN-Au-P^tBuPh₂ (1), and NN-Au-P^tBu₂Ph (2). C' corresponds to an analogous carbon atom in another independent structure of NN-Au-P^tBu₂Ph.

Compounds	Contacts and Distances	<i>d</i> , Å	<i>d</i> -VdW, Å	Symm. Op.
NN-Au-PPh ₃	<i>i</i> (C23–H25...O2)	2.590	−0.130	2− <i>x</i> ,− <i>y</i> ,1− <i>z</i>
	<i>ii</i> (C23–H25...N2)	2.679	−0.071	2− <i>x</i> ,− <i>y</i> ,1− <i>z</i>
	<i>iii</i> (C23–H25...C1)	2.797	−0.103	2− <i>x</i> ,− <i>y</i> ,1− <i>z</i>
	<i>iv</i> (C21...C22)	3.286	−0.114	2− <i>x</i> ,− <i>y</i> ,1− <i>z</i>
	<i>v</i> (C7–H12...O1)	2.416	−0.304	1− <i>x</i> ,−1/2+ <i>y</i> ,1/2− <i>z</i>
	<i>vi</i> (C4–H2...O1)	2.622	−0.098	1− <i>x</i> ,−1/2+ <i>y</i> ,1/2− <i>z</i>
	<i>vii</i> (C15–H18...C24)	2.878	−0.022	2− <i>x</i> ,1− <i>y</i> ,1− <i>z</i>
	<i>viii</i> (C12–H16...O1)	2.322	−0.398	<i>x</i> ,1/2− <i>y</i> ,−1/2+ <i>z</i>
	<i>ix</i> (C12...O1)	3.031	−0.189	<i>x</i> ,1/2− <i>y</i> ,−1/2+ <i>z</i>
	<i>x</i> (C17–H20...O2)	2.459	−0.261	<i>x</i> ,1/2− <i>y</i> ,−1/2+ <i>z</i>
	<i>xi</i> (O2...C17)	3.085	−0.135	<i>x</i> ,1/2− <i>y</i> ,−1/2+ <i>z</i>
NN-Au-P ^t BuPh ₂ *	<i>i</i> (C16–H2...O2)	2.540	−0.180	1− <i>x</i> ,1− <i>y</i> , <i>z</i>
	<i>ii</i> (H13...H13')	2.363	−0.037	1− <i>x</i> ,1− <i>y</i> , <i>z</i>
	<i>iii</i> (C23–H6...O2)	2.534	−0.186	−1/2+ <i>x</i> ,1/2− <i>y</i> ,1− <i>z</i>
NN-Au-P ^t Bu ₂ Ph **	<i>i</i> (C6'–H39...O1')	2.540	−0.180	− <i>x</i> ,1− <i>y</i> ,− <i>z</i>
	<i>ii</i> (C8'–H38...O1')	2.593	−0.127	− <i>x</i> ,1− <i>y</i> ,− <i>z</i>
	<i>iii</i> (C11–H13...O1)	2.705	−0.015	1− <i>x</i> ,2− <i>y</i> ,1− <i>z</i>
	<i>iv</i> (C22'–H58...O1)	2.394	−0.326	<i>x</i> , <i>y</i> , <i>z</i>
	<i>v</i> (C10'–H47...O1)	2.580	−0.140	<i>x</i> , <i>y</i> , <i>z</i>
	<i>vi</i> (C15...H61)	2.845	−0.055	<i>x</i> , <i>y</i> , <i>z</i>
	<i>vii</i> (O2...H55–C19')	2.632	−0.088	1− <i>x</i> ,1− <i>y</i> ,1− <i>z</i>
	<i>viii</i> (O2...C19')	3.217	−0.003	1− <i>x</i> ,1− <i>y</i> ,1− <i>z</i>
	<i>ix</i> (O2...C20')	3.165	−0.055	1− <i>x</i> ,1− <i>y</i> ,1− <i>z</i>
	<i>x</i> (O2...H56–C20')	2.528	−0.192	1− <i>x</i> ,1− <i>y</i> ,1− <i>z</i>
	<i>xi</i> (O2'...H8–C16)	2.581	−0.139	<i>x</i> , <i>y</i> ,1+ <i>z</i>
	<i>xii</i> (O2'...H23–C22)	2.430	−0.290	<i>x</i> , <i>y</i> ,1+ <i>z</i>

* Short contacts with solvate molecules are not included. ** Other short contacts of types H...H and C...H are not included.

Figure 4. Cont.

Figure 4. Short intermolecular contacts and interatomic distances in crystals of NN-Au-PPh₃ [4]: dimer formation (a), binding of dimers into a layer (b), and binding the layers into a 3D framework ((c) red dashed lines).

Figure 5. Cont.

Figure 5. Short intermolecular contacts and interatomic distances in crystals of NN-Au-P^tBuPh₂ (1): dimer formation (a), binding of the dimers into a 3D framework via contacts *iii* and bridging solvate molecules (b).

The presence of two independent molecules in the crystal structure of derivative 2 and the absence of solvate molecules result in an intricate and complex network of intermolecular contacts. To clearly show these contacts, it is reasonable to isolate in the structure a pair of dimers A and B consisting of independent molecules (Figure 6a). One of the dimers is formed by the binding of molecules via four van der Waals interactions of the C_{Me}–H···O1' type (contacts *i* and *ii*). Another dimer is also formed due to short contacts C_{Me}–H···O1 (contacts *iii*) with the participation of the *tert*-butyl group. The oxygen atom engages in two more intermolecular contacts (*iv* and *v*) with the H atoms of the phenyl ring and the *tert*-butyl group, thereby causing the binding of the dimers into alternating ABAB chains. In turn, the chains are linked together into a 3D framework through short contacts *viii*–*xii* with the participation of oxygen atoms of the nitroxide groups (Figure 6b).

Figure 6. Cont.

Figure 6. Short intermolecular contacts and interatomic distances in crystals of NN-Au-P^tBu₂Ph (2): two dimers A and B consisting of independent molecules (a), binding of the dimers into a 3D framework via contacts viii-xii (b).

3.2. ESR Spectra of NN-Au-P^tBuPh₂ and NN-Au-P^tBu₂Ph

Figure 7 shows experimental ESR spectra of NN-Au-P^tBuPh₂ and NN-Au-P^tBu₂Ph (recorded at room temperature in a dilute degassed toluene solution) and their modeling in Winsim v.0.96 [16] by the procedure described earlier [17]. Isotropic *g* values were determined using solid DPPH as the standard, and accuracy rates of determining the hyperfine coupling constants and *g* values are estimated as 0.005 mT and 0.0001, respectively. The spectra are very similar and feature dominant couplings with two equivalent nitrogen atoms and one phosphorus atom producing a pattern consisting of a quintet of doublets with *g* values somewhat higher than typical for purely organic R-NNs. The magnetic parameters for NN-Au-P^tBuPh₂ are as follows: *A*(2N) = 0.795 mT, *A*(P) = 0.225 mT, and *g*_{iso} = 2.0071; for NN-Au-P^tBu₂Ph: *A*(2N) = 0.800 mT, *A*(P) = 0.215 mT, and *g*_{iso} = 2.0068. No finer couplings could be resolved in the spectra probably because bulky substituents impeded radical rotation in solution, thus resulting in an incomplete average of interfering anisotropic interactions. As with previous works [1,4], no signs of couplings with gold were found in the spectra, although the only stable natural isotope, ¹⁹⁷Au, is magnetic, with *I* = 3/2, which indicates an identical zero *s*-character of SOMO in Au(I).

Figure 7. Simulated (top) and observed (bottom) ESR spectra for a solution of NN-Au-P^tBuPh₂ or NN-Au-P^tBu₂Ph in toluene.

3.3. Electrochemical Properties of NN-Au-P^tBuPh₂ and NN-Au-P^tBu₂Ph

To obtain more information about the electronic properties of NN metalloorganic complexes NN-Au-P^tBuPh₂ and NN-Au-P^tBu₂Ph, their electrochemical analysis was performed. Figure 8 depicts cyclic voltammograms of the compounds synthesized in a CH₂Cl₂ solution. The two compounds have similar values of oxidation potential: $E_{1/2}^{ox} = -0.03$ V for NN-Au-P^tBuPh₂ and $E_{1/2}^{ox} = -0.06$ V for NN-Au-P^tBu₂Ph (vs. the Fc/Fc⁺ redox couple), which is comparable to that of NN-Au-PPh₃ ($E_{1/2}^{ox} = -0.07$ V). Overall, the organogold paramagnets have low oxidation potential as compared, for example, to that of NN-H (+0.38 V) [18]. This specific feature of the NN gold derivatives, as shown above, drastically affects the crystal packing of radicals.

Figure 8. Cyclic voltammetric profiles of an NN solution: NN-Au-P^tBuPh₂ (black) and NN-Au-P^tBu₂Ph (red) (0.1 M Bu₄NPF₆ as the supporting electrolyte in dichloromethane at a scan rate of 100 mV·s^{−1}; the potentials are presented relative to the Fc⁺/Fc redox couple).

3.4. Pd(0)-Mediated Cross-Coupling Reactions of NN-Au-P^tBu₂Ph

To investigate the relation between the structure of the gold complexes of the phosphine ligand and their reactivity, we carried out the reaction of NN-Au-PPh₃ with *p*-bromonitrobenzene. The following conditions were applied: *p*-BrC₆H₄NO₂ (1.0 eq.), NN-Au-PPh₃ (1.0 eq.), and Pd(PPh₃)₄ (0.1 eq.) were dissolved in toluene under argon, and the mixture was heated at 70 °C; the total conversion was achieved after 3 h, and the product yield was 88%. Next, the cross-coupling reactions of NN-Au-P^tBu₂Ph and

NN-Au-P^tBuPh₂ were conducted in a similar manner. As it turned out, the reaction times were almost the same (~3.5 h), and the cross-coupling products were obtained in similar yields (84–88%; Scheme 1). Therefore, the presence of *tert*-butyl substituents in the phosphine moiety of NN-Au-P^tBu₂Ph does not influence the cross-coupling process.

Scheme 1. Cross-coupling reactions of **1**, **2**, and NN-Au-PPh₃ with *p*-BrC₆H₄NO₂.

4. Conclusions

We synthesized new gold metalloorganic derivatives of an NN, i.e., NN-Au-P^tBuPh₂ and NN-Au-P^tBu₂Ph. Molecular and crystal structures of these compounds were solved by XRD analysis; the paramagnets were characterized by ESR spectroscopy, cyclic voltammetry, and IR and UV/VIS spectroscopy. According to the XRD analysis, the NN moiety is prone to form a large number of short intermolecular contacts. This propensity reflects the anionic nature of the paramagnetic NN group, as demonstrated by a significantly lower oxidation potential of the gold derivatives in comparison with purely organic derivatives of NN radicals.

Compounds NN-Au-P^tBuPh₂ and NN-Au-P^tBu₂Ph as well as NN-Au-PPh₃ were shown to react with *p*-bromonitrobenzene in the presence of Pd(PPh₃)₄ in toluene virtually at the same rate to give the cross-coupling product with comparable yields. Thus, the steric hindrances created by bulky groups at the phosphorus atom barely affect the cross-coupling reaction of paramagnetic gold-organic compounds of type NN-Au-PR₃ with the selected aryl bromide.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4352/10/9/770/s1>, the supplementary crystallographic data.

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