chemistry proceedings

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Proceeding Paper

Palladium Cyclometallated Compounds: Evaluation of Their Catalytic Activity in Cross-Coupling Reactions †

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† Presented at the 2nd International Electronic Conference on Catalysis Sciences—A Celebration of Catalysts 10th Anniversary, 15–30 October 2021; Available online: https://eccs2021.sciforum.net/.

Abstract: Catalysts are substances that can increase the speed of a chemical reaction and are often used in the chemical industry. Palladium is one of the most widely used metal centers in metal-based catalysts, and a lot of palladium complexes have been extensively used in many reactions, particularly in cross-coupling reactions with a carbon−carbon bond formation. All their possible applications as catalysts, along with their uses in biological assays as anticancer agents, make these family of complexes very interesting and highly studied, allowing the modification of the ligands around the metal and the extreme modulation of their properties. Herein we report the synthesis of several palladium cyclometallated compounds with thiosemicarbazone ligands and bis(diphenylphosphino)methane (dppm). Additionally, we evaluate their catalytic activity in a Suzuki−Miyaura cross-coupling reaction, using 4-bromoacetophenone and phenylboronic acid as reagents and following the reaction with ^{1}H-NMR spectroscopy. A final comparison between the catalytic conversions and the complexes allows us to propose the best structure for a catalytic purpose in these conditions.

Keywords: cyclometallation; palladium; diphosphine; catalysis; Suzuki−Miyaura; cross-coupling

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Citation: Rúa-Sueiro, M.; Munín-Cruz, P.; Bermúdez-Fernández, S.; Vila, J.M. Palladium Cyclometallated Compounds: Evaluation of Their Catalytic Activity in Cross-Coupling Reactions. *Chem. Proc.* **2022**, *6*, 10. https://doi.org/10.3390/ECCS2021-11034

Academic Editor: Keith Hohn

Published: 12 July 2022

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1. Introduction

The chemistry of transition metals has been extensively studied over the years [1,2]. The high number of different metals and the ligands that can coordinate around them make this kind of complex very extensive with different properties and applications in coordinative and organometallic chemistry.

Among all these metals, palladium is one of the most interesting. Its coordinative ability to many donor atoms [3–5], including carbon atoms to synthesized cyclometallated compounds [6–8], makes this metal an excellent choice. The square-planar geometry facilitates the coordination of multidentate ligands [9,10], creating very stable complexes.

Cyclometallated compounds with palladium, using thiosemicarbazone ligands, are reported in this research work [11–15]. We show the catalytic activity for these ligands with different metal complexes [16]. The catalytic activity of all species synthesized is discussed for the Suzuki−Miyaura's reaction.

2. Experimental

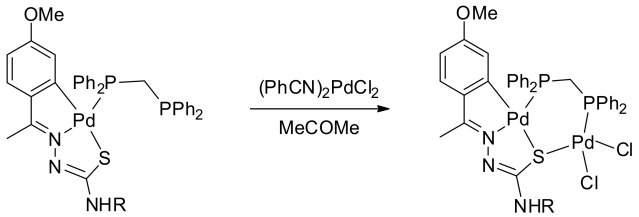
The reactions to obtain the thiosemicarbazone ligands, tetranuclear compounds with palladium and reaction of these compounds with dppm were carried out following the procedure we reported earlier [17].

*Synthesis of Homodinuclear Compounds (***10–12***)*

Compounds **7–9** (15 mg) and bis(benzonitrile)palladium (II) chloride (quantities shown in Table 1) were added under nitrogen in a deoxygenated solution of acetone (Scheme 1). After stirring for 24 h at room temperature, the solvent was removed under a reduced pressure, and the residue was treated with dichloromethane-hexane, centrifugated and dried under a vacuum.

Table 1. Summary of yields and colors of complexes **10–12**.

Compound	Reagent	R	$(PhCN)_2PdCl_2$/mg	Yield/%	Appearance
10	7	H	8.1	60	Red solid
11	8	Me	7.9	52	Orange solid
12	9	Et	7.8	55	Orange solid



Scheme 1. Formation of dinuclear compounds.

3. Results and Discussion

The previous synthetic route is shown in Scheme A1 and NMR spectra are included in Figures A1 and A2. The general procedures and characterization data are listed in Appendix B.

The comparison of the ^{1}H NMR spectra between the dinuclear compounds (**10–12**) with the previous ones (**7–9**) does not show very significant changes. The most remarkable one is the high field shift of the PCH_2P protons, due to the second metal coordination to the free phosphorus atom. This fact is supported with the ^{31}P-{^{1}H} NMR spectrum of 10 because two doublets appear downfield, caused by the coordination of the two phosphorus atoms to different palladium metal centers (as shown in Figure 1).

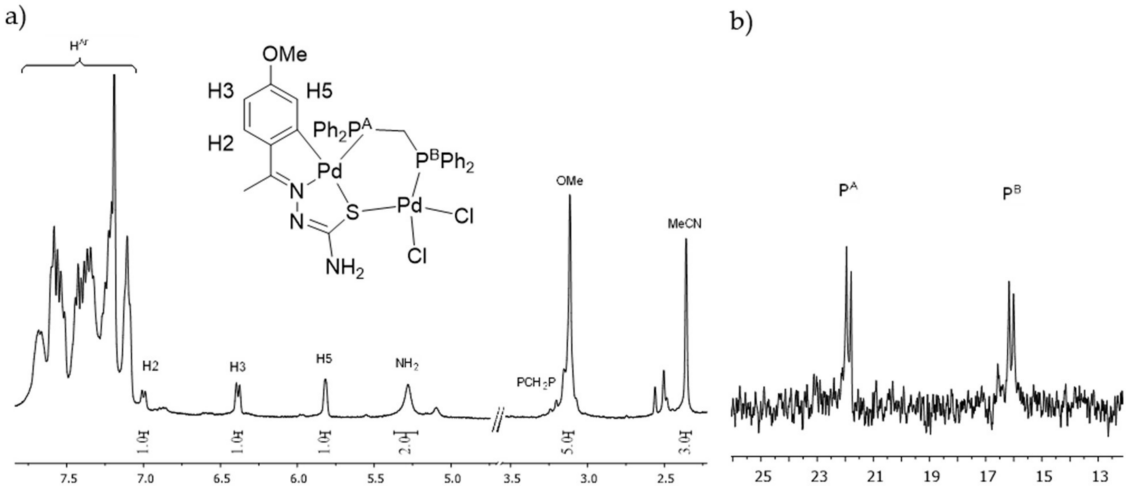
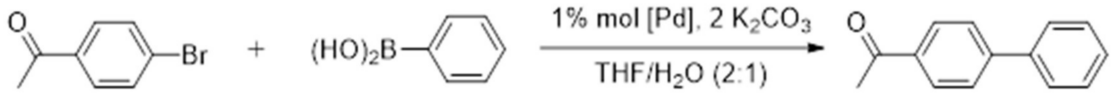


Figure 1. NMR spectra of compound 10 in $CDCl_3$. (**a**) ^{1}H NMR spectrum and (**b**) ^{31}P-{^{1}H} NMR spectrum.

4. Catalytic Conversion

The Suzuki−Miyaura reaction was carried out using 4-bromoacetophenone and phenylboronic acid as reagents (see Scheme 2). Aliquots were taken during the reaction, and results were monitored with ^{1}H NMR spectroscopy as shown in Figure 2.



Scheme 2. Suzuki−Miyaura's reaction scheme.

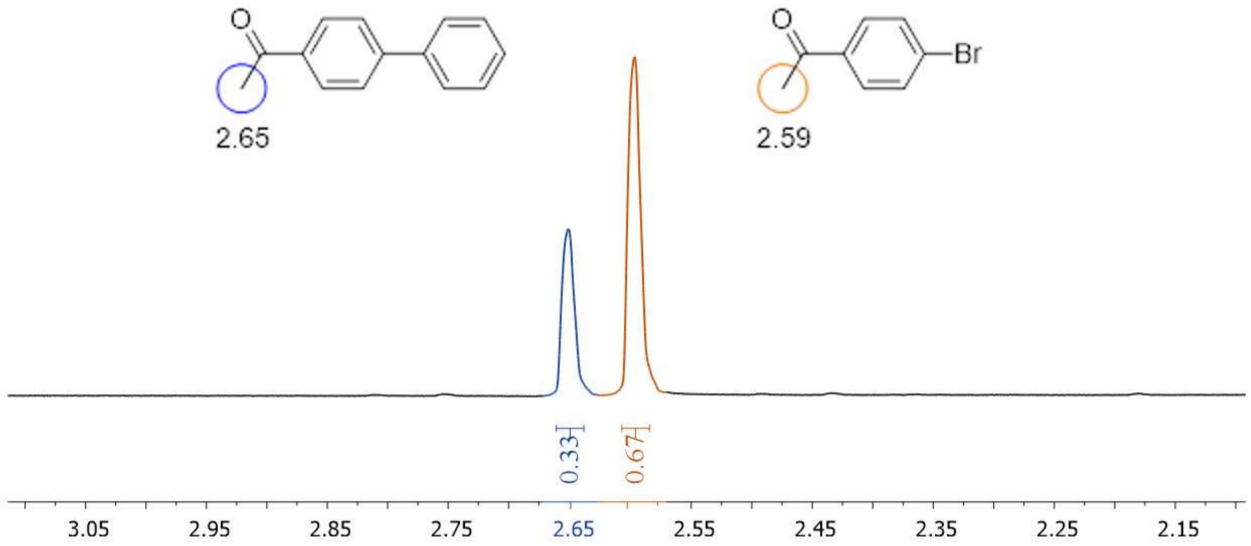


Figure 2. Example of a 33% conversion rate for a catalytic reaction.

Conversion results are shown in Table 2 for all reactions.

Table 2. Results obtained for catalytic assays.

Compound	Reaction Time/h	Conversion/%
4	24	0
5	24	15
6	24	18
7	24	12
8	24	17
9	24	22
10	2	45
	8	89
	24	98
11	2	36
	8	74
	24	97
12	2	43
	8	65
	24	96

Aliquots in **4**–**9** reactions are not listed due to the low conversion. Reactions were carried out using 4-bromoacetophenone (0.2 mmol), phenylboronic acid (1.2 eq.), catalyst (1 mol%) and potassium carbonate (2 eq.) in TFH:H_2O (2:1) at 80 °C. Conversion was determined by ^{1}H NMR spectroscopy.

The results show that the dinuclear compounds are extremely good catalysts, probably due to the Pd−Cl bond. The bond lability allows these compounds to be very effective in these conditions.

Compounds **4**–**9** show poor catalytic activity in these conditions, especially compared to their homodinuclear counterparts.

5. Conclusions

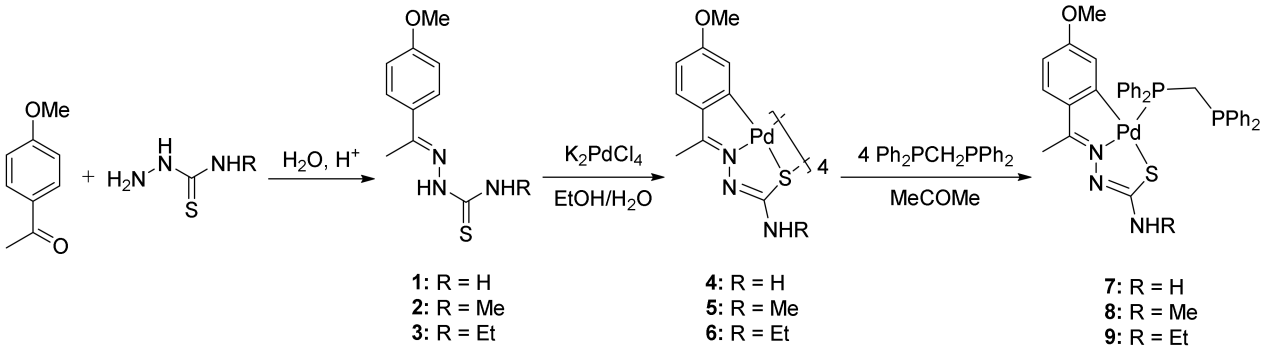
1. Homodinuclear compounds were satisfactorily synthesized, showing a six-membered ring with two palladium atoms.
2. NMR spectra of compounds **10**–**12** confirm the product structure.
3. Catalytic assays were performed for compounds **4**–**12**.
4. Catalytic results show that the dinuclear compounds are better catalysts for the Suzuki−Miyaura reaction.

Author Contributions: Conceptualization, M.R.-S. and P.M.-C.; methodology, M.R.-S. and S.B.-F.; software, M.R.-S.; validation, M.R.-S., P.M.-C. and S.B.-F.; formal analysis, M.R.-S.; investigation, M.R.-S. and P.M.-C.; resources, J.M.V.; writing—original draft preparation, M.R.-S. and J.M.V.; writing—review and editing, M.R.-S.; visualization, M.R.-S. and P.M.-C.; supervision, J.M.V.; project administration, M.R.-S. and J.M.V.; funding acquisition, J.M.V.. All authors have read and agreed to the published version of the manuscript.

Acknowledgments: The authors thank funding from Xunta de Galicia (Galicia, Spain) under the Grupos de Referencia program (GRC 2019/014).

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A



1: R = H
2: R = Me
3: R = Et

4: R = H
5: R = Me
6: R = Et

7: R = H
8: R = Me
9: R = Et

Scheme A1. Synthetic route of compounds **1**–**9**.

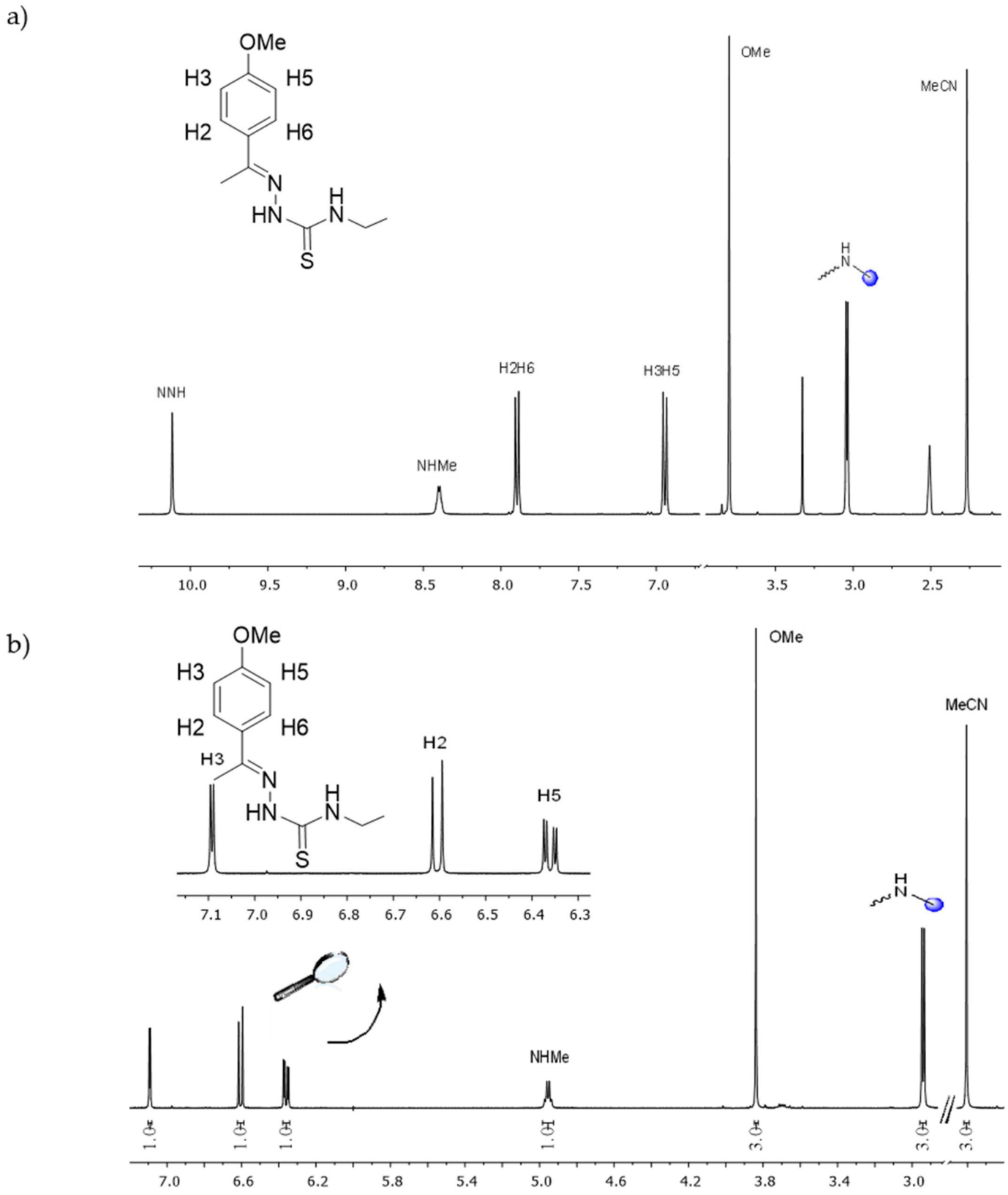


Figure A1. ^{1}H spectra in DMSO-d_6 of compound **3** (**a**) and **5** (**b**).

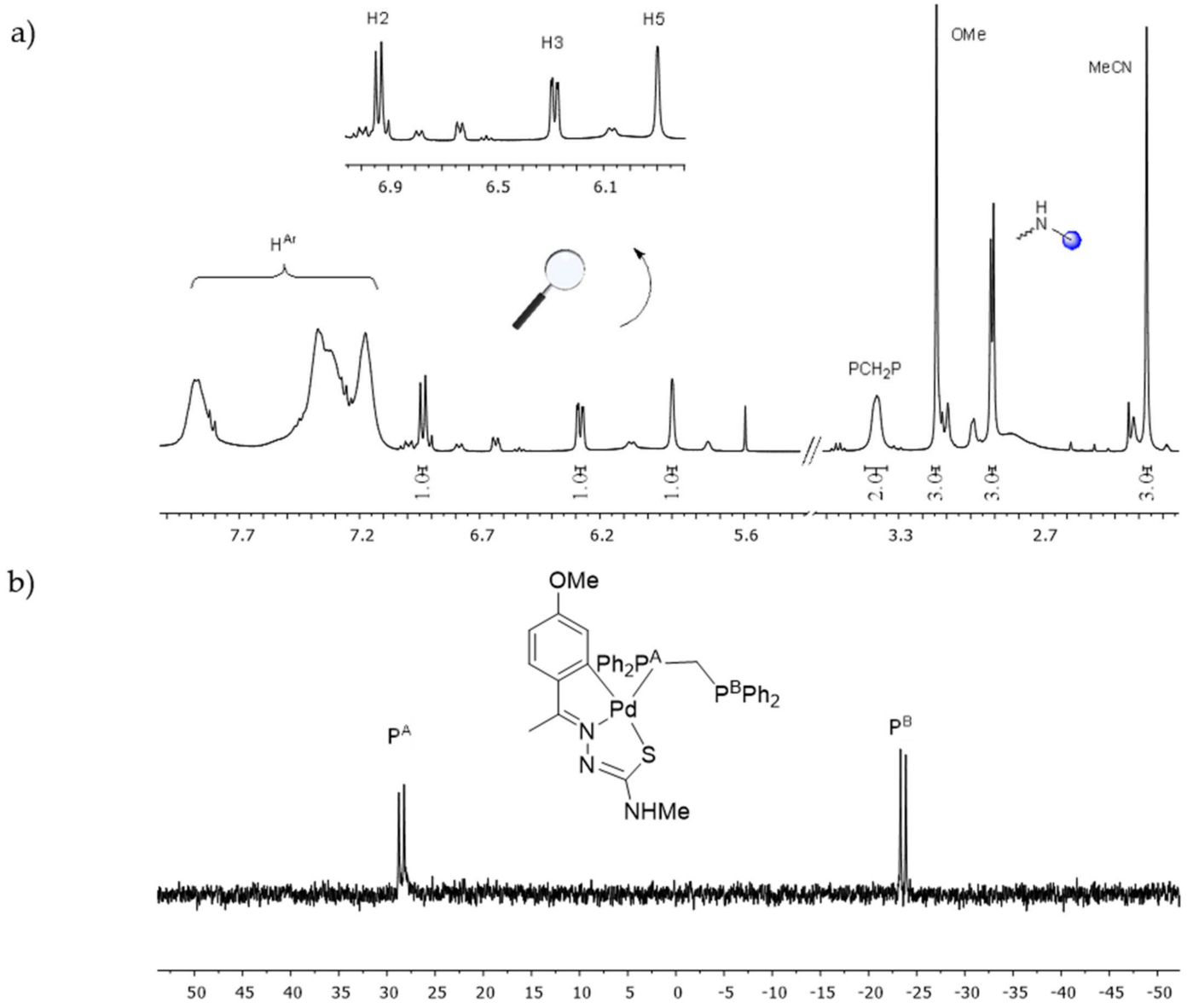


Figure A2. NMR spectra of compound **8** in MeCOMe-d_6. (**a**) ^{1}H NMR spectrum and (**b**) ^{31}P–{^{1}H} NMR spectrum.

Appendix B

Elemental analyses were performed with a Thermo Finnigan analyzer, model Flash 1112. IR spectra were recorded on a Jasco model FT/IR-4600 spectrophotometer equipped with an ATR model ATR-PRO ONE. ^{1}H NMR spectra and ^{31}P-{^{1}H} NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 400.14 MHz (^{1}H NMR) and 161.91 MHz (^{31}P-{^{1}H} NMR), using 5 mm o.d. tubes. Chemical shifts, in ppm, are reported downfield relative to TMS using the solvent signal as a reference (DMSO-d_6 = 2.50, MeCOMe-d_6 = 2.05, $CDCl_3$ = 7.26) in ^{1}H NMR spectra and relative to external H_3PO_4 (85%) in ^{31}P-{^{1}H} NMR. Coupling constants are reported in Hz.

Compound 1

Yield: 535.3 mg, 90%. Anal. Theorical: C: 53.8, H: 5.9, N: 18.8, S: 14.4%; found: C: 52.7, H: 5.9, N: 18.1, S: 15.0%; $C_{10}H_{13}N_3OS$ (223.29 g/mol); IR (cm^{-1}): ν(C=N) 1606, ν̃(C=S) 826. ^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm): 10.11 (s, 1H, NNH), 8.20 (s, 1H, NH_2), 7.88 (d, 1H, H2/H6, N = 8.8), 7.85 (s, 1H, NH_2), 6.92 (d, 2H, H3/H5, N = 8.8), 3.78 (s, 3H, OMe), 2.26 (s, 3H, MeC=N).

Compound 2

Yield: 619.5 mg, 98%. Anal. Theorical: C: 55.7, H: 6.4, N: 17.7, S: 13.5%; found: C: 55.6, H: 6.6, N: 17.5, S: 13.4%; $C_{11}H_{15}N_3OS$ (237.32 g/mol); IR (cm^{-1}): ν(C=N) 1607, ν(C=S) 836. ^1H NMR (400 MHz, DMSO-d_6, δ/ppm, J/Hz): 10.11 (s, 1H, NNH), 8.39 (q, 1H, NHMe, ^3J = 4.5), 7.89 (d, 2H, H2/H6, N = 8.8), 6.94 (d, 2H, H3/H5, N = 8.8), 3.79 (s, 3H, OMe), 3.03 (d, 3H, NHMe, ^3J = 4.6), 2.26 (s, 3H, MeC=N).

Compound 3

Yield: 589.1 mg, 88%. Anal. Theorical: C: 57.3, H: 6.8, N: 16.7, S: 12.8%; found: C: 57.4, H: 6.8, N: 16.7, S: 13.0%; $C_{12}H_{17}N_3OS$ (251.35 g/mol); IR (cm^{-1}): ν(C=N) 1595, ν(C=S) 829. ^1H NMR (400 MHz, DMSO-d_6, δ/ppm, J/Hz): 10.03 (s, 1H, NNH), 8.43 (t, 1H, NHEt, ^3J = 5.7), 7.88 (d, 2H, H2/H6, N = 8.8), 6.94 (d, 2H, H3/H5, N = 8.8), 3.79 (s, 3H, OMe), 3.61 (m, 2H, $NHCH_2CH_3$), 2.26 (s, 3H, MeC=N), 1.15 (t, 3H, $NHCH_2CH_3$, ^3J = 7.1).

Compound 4

Yield: 112.9 mg, 75%. Anal. Theorical: C: 36.7, H: 3.4, N: 12.8, S: 9.8%; found: C: 36.7, H: 3.6, N: 12.7, S: 9.6%; $C_{40}H_{44}N_{12}O_4Pd_4S_4$ (1310.79 g/mol); IR (cm^{-1}): ν(C=N) 1577. ^1H NMR (400 MHz, DMSO-d_6, δ/ppm, J/Hz): 6.93 (d, 1H, H5, ^4J = 1.9), 6.53 (m, 3H, H2/NH_2), 6.30 (dd, 1H, H3, ^3J = 8.3, ^4J = 1.9), 3.75 (s, 3H, OMe), 1.76 (s, 3H, MeC=N).

Compound 5

Yield: 122.5 mg, 78%. Anal. Theorical: C: 38.7, H: 3.8, N: 12.3, S: 9.4%; found: C: 38.6, H: 3.9, N: 12.0, S: 9.1%; $C_{44}H_{52}N_{12}O_4Pd_4S_4$ (1366.90 g/mol); IR (cm^{-1}): ν(C=N) 1571. ^1H NMR (400 MHz, DMSO-d_6, δ/ppm, J/Hz): 7.09 (d, 1H, H5, 4J = 2.6), 6.60 (d, 1H, H2, ^3J = 8.4), 6.36 (dd, 1H, H3, ^3J = 8.4, ^4J = 2.6), 4.95 (q, 1H, NHMe, ^3J = 4.8), 3.84 (s, 3H, OMe), 2.94 (d, 3H, NHMe, ^3J = 4.9), 1.81 (s, 3H, MeC=N).

Compound 6

Yield: 140.6 mg, 86%. Anal. Theorical: C: 40.5, H: 4.3, N: 11.8, S: 9.0%; found: C: 40.5, H: 4.4, N: 11.9, S: 8.9%; $C_{48}H_{60}N_{12}O_4Pd_4S_4$ (1423.01 g/mol); IR (cm^{-1}): ν(C=N) 1572. ^1H NMR (400 MHz, DMSO-d_6, δ/ppm, J/Hz): 7.18 (d, 1H, H5, ^4J = 2.5), 6.81 (m, 1H, NHEt), 6.76 (d, 1H, H2, ^3J = 8.4), 6.55 (dd, 1H, H3, ^3J = 8.4, ^4J = 2.5), 4.00 (s, 3H, OMe), 2.75 (m, 2H, $NHCH_2CH_3$), 2.01 (s, 3H, MeC=N), 1.30 (t, 3H, $NHCH_2CH_3$, ^3J = 7.0).

Compound 7

Yield: 71.7 mg, 66%. Anal. Theorical: C: 59.0, H: 4.7, N: 5.9, S: 4.5%; found: C: 59.0, H: 4.9, N: 5.6, S: 4.3 %; $C_{35}H_{33}N_3OP_2PdS$ (712.10 g/mol); IR (cm^{-1}): ν(C=N) 1575. ^1H NMR (400 MHz, MeCOMe-d_6, δ/ppm, J/Hz): 7.94–7.15 (m, 20H, H^{Ar}), 6.89 (d, 1H, H2, ^3J = 8.4), 6.25 (d, 1H, H3, ^3J = 8.2), 5.87 (m, 1H, H5), 5.73 (s, 2H, NH_2) 3.39 (m, 2H, PCH_2P), 3.14 (s, 3H, OMe), 2.18 (s, 3H, MeC=N). ^{31}P-{^1H} NMR (400 MHz, MeCOMe-d_6, δ/ppm, J/Hz): 28.20 (d, P^A, ^2J = 87.9), -23.55 (d, P^B, ^2J = 87.9).

Compound 8

Yield: 79.7 mg, 75%. Anal. Theorical: C: 59.6, H: 4.9, N: 5.8, S: 4.4%; found: C: 59.3, H: 4.8, N: 5.6, S: 4.3%; $C_{36}H_{35}N_3OP_2PdS$ (726.12 g/mol); IR (cm^{-1}): ν(C=N) 1578. ^1H NMR (400 MHz, MeCOMe-d_6, δ/ppm, J/Hz): 7.87–7.18 (m, 20H, H^{Ar}), 6.93 (d, 1H, H2, ^3J = 8.4), 6.28 (dd, 1H, H3, ^3J = 8.4, ^4J = 2.3), 5.89 (m, 1H, H5), 3.40 (m, 2H, PCH_2P), 3.14 (s, 3H, OMe), 2.91 (d, 3H, NHMe, ^3J = 4.8), 2.35 (s, 3H, MeC=N). ^{31}P-{^1H} NMR (400 MHz, MeCOMe-d_6, δ/ppm, J/Hz): 28.53 (d, P^A, ^2J = 87.4), -23.58 (d, P^B, ^2J = 87.4).

Compound 9

Yield: 74.9 mg, 72%. Anal. Theorical: C: 60.0, H: 5.0, N: 5.7, S: 4.3%; found: C: 60.2, H: 5.1, N: 5.3, S: 4.2%; $C_{37}H_{37}N_3OP_2PdS$ (740.15 g/mol); IR (cm^{-1}): ν(C=N) 1577. ^1H NMR (400 MHz, MeCOMe-d_6, δ/ppm, J/Hz): 7.91–7.14 (m, 20H, H^{Ar}), 6.92 (d, 1H, H2, ^3J = 8.4), 6.27 (d, 1H, H3, ^3J = 8.4), 5.89 (m, 1H, H5), 3.40 (m, 5H, PCH_2P/$NHCH_2CH_3$), 3.14 (s, 3H, OMe), 2.23 (s, 3H, MeC=N), 1.22 (t, 3H, $NHCH_2CH_3$, ^3J = 7.4). ^{31}P-{^1H} NMR (400 MHz, MeCOMe-d_6, δ/ppm, J/Hz): 28.57 (d, P^A, ^2J = 86.7), -23.57 (d, P^B, ^2J = 86.7).

Compound 10

Yield: 11.2 mg, 60%. Anal. Theorical: C: 47.3, H: 3.7, N: 4.7, S: 3.6 %; found: C: 46.2, H: 3.7, N: 4.3, S: 3.4%; $C_{35}H_{33}Cl_2N_3OP_2Pd_2S$ (889.41 g/mol); IR (cm^{-1}): ν(C=N) 1578. ^1H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 7.92–7.11 (m, 20H, H^{Ar}), 7.00 (d, 1H, H2, ^3J = 8.0),

6.39 (d, 1H, H3, ^{3}J = 8.1), 5.82 (m, 1H, H5), 5.28 (s, 2H, NH_2), 3.12 (m, 5H, PCH_2P/OMe), 2.36 (s, 3H, MeC=N). ^{31}P-{^{1}H} NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 21.87 (d, P^A, ^{2}J = 26.0), 16.10 (d, P^B, ^{2}J = 26.0).

Compound 11

Yield: 9.7 mg, 52%. Anal. Theorical: C: 47.9, H: 3.9, N: 4.7, S: 3.6%; found: C: 46.7, H: 3.6, N: 4.4, S: 3.3%; $C_{36}H_{35}Cl_2N_3OP_2Pd_2S$ (903.44 g/mol); IR (cm^{-1}): ν(C=N) 1573. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 7.94–7.15 (m, 20H, H^{Ar}), 6.92 (d, 1H, H2, ^{3}J = 8.0), 6.43 (d, 1H, H3, ^{3}J = 8.0), 5.87 (m, 1H, H5), 4.89 (m, 1H, NHMe), 3.16 (m, 5H, PCH_2P/OMe), 3.03 (m, 3H, NHMe), 2.45 (s, 3H, MeC=N). ^{31}P-{^{1}H} NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 21.69 (d, P^A, ^{2}J = 26.9), 15.71 (d, P^B, ^{2}J = 26.9).

Compound 12

Yield: 10.2 mg, 55%. Anal. Theorical: C: 48.4, H: 4.1, N: 4.6, S: 3.5%; found: C: 46.5, H: 3.7, N: 4.4, S: 3.4%; $C_{37}H_{37}Cl_2N_3OP_2Pd_2S$ (917.47 g/mol); IR (cm^{-1}): ν(C=N) 1576. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 7.92–7.10 (m, 20H, H^{Ar}), 6.99 (d, 1H, H2, ^{3}J = 7.8), 6.38 (d, 1H, H3, ^{3}J = 7.8), 5.83 (m, 1H, H5), 5.17 (m, 1H, NHEt), 3.43 (m, 2H, $NHCH_2CH_3$), 3.12 (m, 5H, PCH_2P/OMe), 2.37 (s, 3H, MeC=N), 1.17 (m, 3H, $NHCH_2CH_3$). ^{31}P-{^{1}H} NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 21.70 (d, P^A, ^{2}J = 26.7), 15.70 (d, P^B, ^{2}J = 26.7).

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