



Supporting Information

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SUPPORTING INFORMATION

Coordination Chemistry of Ene-1,1-diamines and a Prototype “Carbodicarbene”

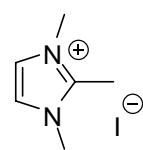
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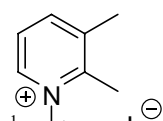
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General : All reactions were carried out in flame-dried glassware under Ar. The solvents were purified by distillation over the drying agents indicated and were transferred under Ar. THF, Et₂O (Mg-anthracene), CH₂Cl₂ (P₄O₁₀), MeCN, Et₃N (CaH₂), MeOH (Mg), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). IR: Nicolet FT-7199 spectrometer, wavenumbers ($\tilde{\nu}$) in cm⁻¹. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker DPX 300 or AV 400 spectrometer in the solvents indicated; ¹H and ¹³C chemical shifts (δ) are given in ppm relative to TMS, ¹⁹F chemical shifts are reported in ppm relative to CF₃COOH, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale. Melting points: Büchi melting point apparatus B-540 (corrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Acros, Fluka, Lancaster, Aldrich) were used as received unless stated otherwise. 2-(Benzoylmethyl)-1-methylimidazole,¹ (*E*)-ethyl 2-(1-methylpyridin-2-ylidene)acetate,² and tetra(dimethylamino)allene,³ were prepared according to literature procedures.

1,2,3-Trimethylimidazolium iodide (2). MeI (4.36 mL, 70 mmol) was added to a solution of 1,2-dimethylimidazole (5.67 g, 60 mmol) in Et₂O (50 ml) and the reaction mixture was stirred at ambient temperature overnight. The white precipitate obtained was filtered off, washed with Et₂O and dried *in vacuo* (13.3 g, 93%). m. p. = 312-314°C; ¹H NMR (400 MHz, d₆-DMSO): δ = 7.60 (s, 2H), 3.76 (s, 6H), 2.50 (s, 3H). ¹³C NMR (100 MHz, d₆-DMSO): δ = 145.1, 122.3, 35.2, 9.7. IR. (neat) ν = 3084, 2943, 1626, 1596, 1552, 1519, 1432, 1260, 1138, 1032, 760, 740 cm⁻¹. HRMS *calcd.* for C₆H₁₁N₂⁺: 111.09214; *found* 111.09222. Elemental analysis *calcd.* (%) for C₆H₁₁N₂I: C 30.27, H 4.66, N 11.77; *found* C 30.32, H 4.62, N 11.82.



1,2,3-Trimethylpyridinium iodide (10). MeI (4.36 mL, 70 mmol) was added to a solution of 2,3-dimethylpyridine (6.8 mL, 60 mmol) in Et₂O (50 ml) and the mixture was stirred at



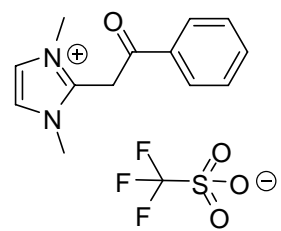
¹ L. A. M. Bastiaansen, A. A. Macco, E. F. Godefroi, *J. Chem. Soc. Chem. Commun.* **1974**, 36.

² R. M. Acheson, J. Woollard, *J. Chem. Soc. Perkin Trans. 1* **1975**, 744-748.

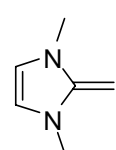
³ H. G. Viehe, Z. Janousek, R. Gompper, D. Lach, *Angew. Chem.* **1973**, 85, 581-582., *Angew. Chem. Int. Ed. Engl.* **1973**, 12, 566-567.

ambient temperature for seven days. The yellow precipitate obtained was filtered off, washed with Et₂O and dried *in vacuo* (13.2 g, 88%). m. p. = 202-204°C; ¹H NMR (400 MHz, d₆-DMSO): δ = 8.84 (d, *J* = 6.1 Hz, 1H), 8.36 (d, *J* = 7.8, 1H), 7.83 (t, *J* = 6.9 Hz, 1H), 4.26 (s, 3H), 2.69 (s, 3H), 2.49 (s, 3H). ¹³C NMR (100 MHz, d₆-DMSO): δ = 155.4, 145.5, 144.1, 138.0, 124.6, 46.8, 19.6, 17.3. IR (neat): $\tilde{\nu}$ = 3036, 3005, 1620, 1494, 1450, 1281, 1027, 995, 813, 694 cm⁻¹. MS (ESI) *calcd.* for C₈H₁₂N⁺: 122.11; *found* 122.13. Elemental analysis *calcd.*(%) for C₈H₁₂NI: C 40.93, H 5.72, N 5.30; *found* C 39.65, H 5.81, N 5.61.

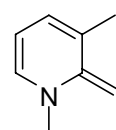
2-(Benzoylmethyl)-1,3-dimethylimidazolium triflate (6). MeOTf (1.19 mL, 10.5 mmol) was added to a suspension of 2-(benzoylmethyl)-1-methylimidazole (2.0 g, 10 mmol) in Et₂O (20 ml) and the mixture was stirred at ambient temperature overnight. The off white precipitate obtained was filtered off, washed with Et₂O and dried *in vacuo* (3.42 g, 94%). m. p. = 125-127°C; ¹H NMR (400 MHz, d₆-acetone): δ = 8.16 (d, *J* = 8.5 Hz, 2H), 7.78 (s, 2H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 2H), 5.35 (s, 2H), 4.00 (s, 6H). ¹³C NMR (100 MHz, d₆-acetone): δ = 193.0, 144.2, 136.6, 135.6, 130.2, 130.0, 124.6, 36.3, 35.7. IR (neat): $\tilde{\nu}$ = 3150, 2951, 1687, 1327, 1254, 1159, 1027, 761, 736, 689 cm⁻¹. HRMS *calcd.* for C₁₃H₁₅N₂O⁺: 215.11789; *found* 215.11775. Elemental analysis *calcd.*(%) for C₁₄H₁₅N₂O₄SF₃: C 46.15, H 4.15, N 7.69; *found* C 46.22, H 4.20, N 7.57.



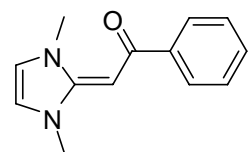
1,3-Dimethyl-2-methylene-2,3-dihydro-1H-imidazole (3). 1,2,3-Trimethylimidazolium iodide (3.57 g, 15 mmol) was added to a suspension of KH (1.2 g, 30 mmol) in Et₂O (50 ml) and the mixture was stirred at ambient temperature for two days in the absence of light. After filtration and removal of the organic solvent *in vacuo*, the desired product was obtained as a white crystalline, very air sensitive solid (1.43 g, 87%). ¹H NMR (300 MHz, d₆-benzene): δ = 5.26 (s, 2H), 2.56 (s, 2H), 2.32 (s, 6H). ¹³C NMR (75 MHz, d₆-benzene): δ = 153.3, 113.2, 40.3, 32.8. HRMS *calcd.* for C₆H₁₀N₂: 110.084399; *found* 110.084215.



1,3-Dimethyl-2-methylene-1,2-dihydropyridine (11). 1,2,3-Trimethylpyridinium iodide (2.50 g, 10 mmol) was added to a suspension of KH (600 mg, 15 mmol) in Et₂O (30 ml) and the mixture was stirred at ambient temperature for 24 h in the absence of light. Insoluble residues were filtered off (and carefully destroyed), and the filtrate was evaporated to give the title compound as a yellow air sensitive oil (1.02 g, 84%). ¹H NMR (400 MHz, d₆-benzene): δ = 5.98 (dd, *J* = 6.1, 0.6 Hz, 1H), 5.89 (d, *J* = 7.0 Hz, 1H), 5.04 (t, *J* = 6.6 Hz, 1H), 3.60 (s, 1H), 3.34 (s, 1H), 2.39 (s, 3H), 1.77 (s, 3H). ¹³C NMR (100 MHz, d₆-benzene): δ = 148.3, 136.1, 128.2, 125.6, 99.0, 70.1, 40.5, 20.3. HRMS *calcd.* for C₈H₁₁N: 121.08915; *found* 121.08921.

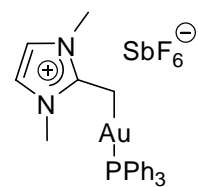


Compound 7. 2-(Benzoylmethyl)-1,3-dimethylimidazolium triflate (1.82 g, 5 mmol) was added to a suspension of KH (240 mg, 6 mmol) in THF (20 ml) and the mixture was stirred overnight at ambient temperature. Evaporation of the organic solvent produces a yellow solid that was extracted with CH₂Cl₂ (2 x 10 mL). The combined extracts were evaporated to give the title compound as a yellow solid (845 mg, 79%). m. p. = 175-176°C; ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.79-7.76 (m, 2H), 7.28-7.26 (m, 3H), 6.59 (s, 2H), 5.00 (s, 1H), 3.51 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ = 178.6, 153.4, 145.2, 130.1, 129.2, 128.3, 119.8, 70.4, 37.2. IR (neat): $\tilde{\nu}$ = 3064, 1573, 1519, 1485, 1429, 1396, 1330, 1212, 878, 701

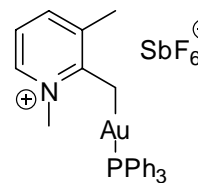


cm⁻¹. HRMS *calcd.* for C₁₃H₁₅N₂O⁺: 215.11789; *found* 215.11780. Elemental analysis *calcd.*(%) for C₁₃H₁₄N₂O: C 72.87, H 6.59, N 13.07; *found* C 72.79, H 6.53, N 13.01.

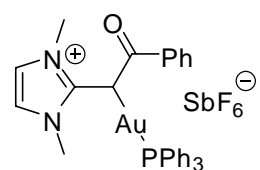
Compound 4. To a suspension of 1,3-dimethyl-2-methylene-2,3-dihydro-1*H*-imidazole (**3**) (22 mg, 0.2 mmol) in THF (2 mL) were added Ph₃PAuCl (98 mg, 0.2 mmol) and NaSbF₆ (51.7 mg, 0.2 mmol). After stirring for 1 h, the solvent was evaporated and the remaining solid suspended in CH₂Cl₂ (10 mL). The suspension was filtered, the filtrate evaporated and the residue triturated with Et₂O (2 x 2 mL) to give the desired complex as an off white solid (143 mg, 89%). m. p. = 166-167°C (decomp.); ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.99-7.45 (m, 15H), 6.79 (s, 2H), 3.60 (s, 6H), 2.32 (d, *J* = 10.3 Hz, 2H). ¹³C NMR (100 MHz, CD₂Cl₂): δ = 157.3 (d, *J* = 5.0 Hz), 134.8 (d, *J* = 13.1 Hz), 132.6 (d, *J* = 2.0 Hz), 130.1 (d, *J* = 11.3 Hz), 120.1, 35.2, 22.1 (d, *J* = 80.2 Hz). IR (neat): $\tilde{\nu}$ = 1576, 1520, 1481, 1436, 1157, 1102, 1029, 748, 710 cm⁻¹. HRMS *calcd.* for C₂₄H₂₅N₂AuP⁺: 569.14154; *found* 569.14177. Elemental analysis *calcd.*(%) for C₂₄H₂₅N₂AuF₆SbP: C 35.80, H 3.13, N 3.48; *found* C 35.70, H 3.21, N 3.27.



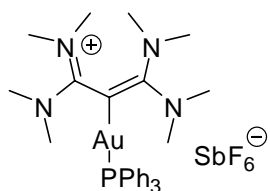
Compound 12. To a suspension of 1,3-dimethyl-2-methylene-1,2-dihydropyridine (**11**) (24 mg, 0.2 mmol) in THF (2 mL) were added Ph₃PAuCl (98 mg, 0.2 mmol) and AgSbF₆ (68.7 mg, 0.2 mmol). After stirring for 1 h, the solvent was evaporated and the remaining solid suspended in CH₂Cl₂ (10 mL). The suspension was filtered, the filtrate evaporated, and the residue triturated with Et₂O (2 x 2 mL) to give the desired complex as a pale grey solid (111 mg, 68%). m. p. = 177-179°C (decomp.); ¹H NMR (300 MHz, CD₃CN): δ = 8.36 (d, *J* = 6.3 Hz, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.68-7.50 (m, 15H), 7.26 (t, *J* = 7.0 Hz, 1H), 4.11 (s, 3H), 2.69 (s, 2H), 2.51 (s, 3H). ¹³C NMR (75 MHz, CD₃CN): δ = 167.1, 140.1 (d, *J* = 11.0 Hz), 133.6 (d, *J* = 13.1 Hz), 133.4, 131.6 (bs), 129.5, 129.1 (d, *J* = 11.3 Hz), 45.0, 34.6 (bs), 19.2. ³¹P NMR (121.5 MHz, CD₃CN): δ = 41.3. IR (neat): $\tilde{\nu}$ = 1624, 1575, 1487, 1436, 1247, 1238, 1101, 990, 979, 799, 749, 693 cm⁻¹. HRMS *calcd.* for C₂₆H₂₆NAuP⁺: 580.14629; *found* 580.14682. Elemental analysis *calcd.*(%) for C₂₆H₂₆AuF₆NPSb: C 38.26, H 3.21, N 1.72; *found* C 39.19, H 3.18, N 1.76.



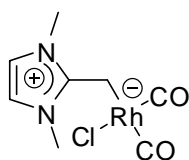
Compound 8. To a solution of compound **7** (43 mg, 0.2 mmol) in THF (2 mL) were added Ph₃PAuCl (98 mg, 0.2 mmol) and AgSbF₆ (68.7 mg, 0.2 mmol). After stirring for 1 h, the solvent was evaporated and the remaining solid suspended in CH₂Cl₂ (10 mL). The suspension was filtered, the filtrate evaporated, and the residue triturated with Et₂O (2 mL) to give the desired complex as an off white solid (154 mg, 85%). m. p. = 190-191°C (decomp.); ¹H NMR (400 MHz, CD₂Cl₂): δ = 8.27 (d, *J* = 7.2 Hz, 2H), 7.70-7.55 (m, 6H), 7.52-7.43 (m, 6H), 7.40-7.30 (m, 6H), 7.17 (s, 2H), 5.41 (d, *J* = 10.3 Hz, 1H), 4.00 (s, 6H). ¹³C NMR (100 MHz, CD₃Cl₃): δ = 198.6, 137.4, 133.9 (d, *J* = 13.9 Hz), 133.6 (d, *J* = 13.4 Hz), 132.4, 131.8, 131.7, 129.1 (d, *J* = 12.0 Hz), 128.8 (d, *J* = 12.0 Hz), 128.4, 128.1, 127.6, 121.1, 48.0 (d, *J* = 62.7 Hz), 36.2. ³¹P NMR (162 MHz, CDCl₃): δ = 39.7. IR (neat): $\tilde{\nu}$ = 1639, 1579, 1505, 1436, 1333, 1209, 1101, 1016, 928, 741, 704 cm⁻¹. MS (ESI) *calcd.* for C₃₁H₂₉N₂AuOP⁺: 673.17; *found* 673.21. Elemental analysis *calcd.*(%) for C₃₁H₂₉AuF₆N₂OPSb: C 40.95, H 3.21, N 3.08; *found* C 41.03, H 3.16, N 3.13.



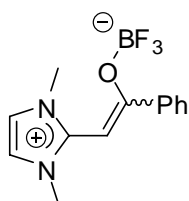
Compound 19. To a suspension of tetra(dimethylamino)allene **18** (64 mg, 0.3 mmol) in THF (2 mL) were added Ph₃PAuCl (98 mg, 0.2 mmol) and NaSbF₆ (51.7 mg, 0.2 mmol). After stirring for 1 h, the solvent was evaporated and the remaining oil washed with Et₂O (2 x 2 mL). The residue was then suspended in CH₂Cl₂ (10 mL), insoluble residues were filtered off and the filtrate was evaporated to a volume of ca. 2 mL. Addition of Et₂O effects the precipitation of the product which was obtained as a very light green solid (130 mg, 72%). m. p. = 162-164°C (decomp.); ¹H NMR (400 MHz, CDCl₃): δ = 7.46-7.34 (m, 15H), 2.90 (s, 24H). ¹³C NMR (75 MHz, CD₂Cl₂): δ = 177.4, 134.3 (d, *J* = 13.6 Hz), 131.9 (d, *J* = 2.2 Hz), 131.0, 130.3, 129.5 (d, *J* = 10.8 Hz), 41.6. ³¹P NMR (162 MHz, CDCl₃): δ = 43.3. IR (neat): $\tilde{\nu}$ = 1504, 1437, 1371, 1099, 1025, 751, 695 cm⁻¹. HRMS *calcd.* for C₂₉H₃₉N₄AuP⁺: 671.25724; *found* 671.25694. Elemental analysis *calcd.*(%) for C₂₉H₃₉N₄AuF₆PSb: C 38.39, H 4.33, N 6.17; *found* C 38.48, H 4.31, N 6.12.



Compound 5. Compound **3** (55 mg, 0.5 mmol) was added to a solution of [RhCl(CO)₂]₂ (97 mg, 0.25 mmol) at 0°C in Et₂O (3 mL) and the resulting mixture was stirred for 1 h at ambient temperature. For work up, the solvent was evaporated and the residue triturated with Et₂O (1 mL) before it was dissolved in THF (3 mL). Pentane was added until the solution became turbid and the mixture was kept overnight at -24 °C, causing the precipitation of the product in form of orange crystals (89 mg, 59%). ¹H NMR (300 MHz, C₆D₆): δ = 5.42 (s, 2H), 2.65 (s, 6H), 1.80 (d, *J* = 2.6 Hz, 2H). IR (neat): $\tilde{\nu}$ = 2040, 1966 cm⁻¹. MS (EI): 304 (7), 276 (13), 248 (9), 212 (21), 110 (100), 95 (28), 68 (21), 54 (17), 42 (22), 28 (50). Elemental analysis *calcd.*(%) for C₈H₁₀ClN₂O₂Rh: C 31.55, H 3.31, N 9.20; *found* C 31.34, H 3.23, N 8.99.



Compound 9. BF₃·OEt₂ (142 mg, 1 mmol) was added to a suspension of compound **7** (214 mg, 1 mmol) at 0°C in Et₂O (5 mL) and the resulting mixture stirred for 2 h at ambient temperature. The solvent was then removed and the residue was triturated with Et₂O (2 x 1 mL). The white solid material consisted of a ~2: 1 diastomeric mixture of the desired product (NMR) (259 mg, 92%), whereas recrystallization from CH₂Cl₂/pentane gave a single isomer (cf. crystal structure analysis). m. p. = 155-156°C. Characteristic data of the major diastereomer: ¹H NMR (400 MHz, CD₃CN): δ = 3.71 (s, 6H), 5.91 (s, 1H), 7.24 (s, 2H), 7.42-7.50 (m, 3H), 7.83-7.90 (m, 2). ¹³C NMR (100 MHz, CD₃CN): δ = 34.9, 85.4, 121.1, 126.7, 127.8, 129.4, 137.6, 164.5. IR (neat): $\tilde{\nu}$ = 3142, 1961, 1632, 1521, 1362, 1071, 1048, 1033, 959, 979, 777, 744, 699 cm⁻¹. MS (EI): 263 (3), 214 (100), 199 (16), 161 (25), 171 (151), 137 (92), 109 (17), 95 (20), 77 (19), 42 (18).



Crystallographic Data

X-ray Crystal Structure Analysis of Complex 4 (CCDC 670972): C₂₅ H₂₇ Au Cl₂ F₆ N₂ P Sb, *M_r* = 890.07 g·mol⁻¹, colorless plate, crystal size 0.24 x 0.20 x 0.12 mm, orthorhombic, space group *Pbca*, *a* = 14.7563(2) Å, *b* = 19.2882(2) Å, *c* = 20.9883(3) Å, *V* = 5973.74(13) Å³, *T* = 100 K, *Z* = 8, *D_{calc}* = 1.979 g·cm⁻³, λ = 0.71073 Å, μ(*Mo-Kα*) = 6.098 mm⁻¹, empirical absorption correction (*T_{min}* = 0.16, *T_{max}* = 0.47), Nonius KappaCCD diffractometer, 2.96 < θ < 33.13, 160764 measured reflections, 11368 independent reflections, 8976 reflections with *I* > 2σ(*I*), Structure solved by direct methods and refined by full-matrix least-squares against *F*² to *R₁* = 0.035 [*I* > 2σ(*I*)], *wR₂* = 0.093, 345 parameters, absolute structure parameter = 0.00, H atoms riding, *S* = 1.065, residual electron density +2.0 / -2.7 e Å⁻³.

X-ray Crystal Structure Analysis of Compound 7 (CCDC 671017): C₁₃H₁₄N₂O, $M_r = 214.26 \text{ g} \cdot \text{mol}^{-1}$, colorless plate, crystal size 0.50 x 0.40 x 0.23 mm, monoclinic, space group $P2_1/c$, $a = 9.8827(11) \text{ \AA}$, $b = 10.3817(11) \text{ \AA}$, $c = 11.2299(12) \text{ \AA}$, $\beta = 90.687(4)^\circ$, $V = 1152.1(2) \text{ \AA}^3$, $T = 200 \text{ K}$, $Z = 4$, $D_{calc} = 1.235 \text{ g} \cdot \text{cm}^3$, $\lambda = 1.54178 \text{ \AA}$, $\mu(\text{Cu-K}\alpha) = 0.635 \text{ mm}^{-1}$, Semi-empirical absorption correction ($T_{min} = 0.75$, $T_{max} = 0.83$), Bruker AXS Proteum X8 diffractometer, $5.80 < \theta < 62.14$, extinction coefficient = 0.031(2), 23242 measured reflections, 1780 independent reflections, 1622 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.044 [I > 2\sigma(I)]$, $wR_2 = 0.124$, 202 parameters, H atoms riding, $S = 1.066$, residual electron density +0.2 / -0.1 e \AA^{-3} .

X-ray Crystal Structure Analysis of Complex 8 (CCDC 670968): C₃₁H₂₉AuF₆N₂OPs, $M_r = 909.25 \text{ g} \cdot \text{mol}^{-1}$, colorless plate, crystal size 0.20 x 0.08 x 0.05 mm, monoclinic, space group $P2_1/c$, $a = 16.8216(2) \text{ \AA}$, $b = 10.14670(10) \text{ \AA}$, $c = 20.0184(2) \text{ \AA}$, $\beta = 111.4830(10)^\circ$, $V = 3179.44 \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 4$, $D_{calc} = 1.900 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 5.571 \text{ mm}^{-1}$, empirical absorption correction ($T_{min} = 0.29$, $T_{max} = 0.75$), Nonius KappaCCD diffractometer, $2.93 < \theta < 27.50$, 63119 measured reflections, 7279 independent reflections, 6985 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.017 [I > 2\sigma(I)]$, $wR_2 = 0.058$, 390 parameters, H atoms riding, $S = 0.993$, residual electron density +0.7 / -1.2 e \AA^{-3} .

X-ray Crystal Structure Analysis of Complex 9 (CCDC 670970): C₁₃H₁₄BF₃N₂O, $M_r = 282.07 \text{ g} \cdot \text{mol}^{-1}$, colorless plate, crystal size 0.25 x 0.22 x 0.13 mm, orthorhombic, space group $P2_12_12_1$, $a = 6.9392(5) \text{ \AA}$, $b = 11.5597(7) \text{ \AA}$, $c = 16.2135(10) \text{ \AA}$, $V = 1300.57(15) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 4$, $D_{calc} = 1.441 \text{ g} \cdot \text{cm}^3$, $\lambda = 1.54178 \text{ \AA}$, $\mu(\text{Cu-K}\alpha) = 1.034 \text{ mm}^{-1}$, empirical absorption correction ($T_{min} = 0.66$, $T_{max} = 0.87$), Bruker AXS Proteum X8 diffractometer, $4.70 < \theta < 70.48$, 28928 measured reflections, 2437 independent reflections, 1866 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.090 [I > 2\sigma(I)]$, $wR_2 = 0.271$, 183 parameters, absolute structure parameter = -0.1(4), H atoms riding, $S = 1.174$, residual electron density +0.4 / -0.6 e \AA^{-3} .

X-ray Crystal Structure Analysis of Complex 12 (CCDC 670971): C₂₆H₂₆AuF₆NPsb, $M_r = 816.16 \text{ g} \cdot \text{mol}^{-1}$, colorless plate, crystal size 0.11 x 0.09 x 0.06 mm, triclinic, space group $P1$, $a = 10.4508(5) \text{ \AA}$, $b = 11.0356(5) \text{ \AA}$, $c = 14.2226(5) \text{ \AA}$, $\alpha = 94.738(2)^\circ$, $\beta = 105.926(2)^\circ$, $\gamma = 117.421(2)^\circ$, $V = 1357.52(10) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 2$, $D_{calc} = 1.997 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 6.508 \text{ mm}^{-1}$, empirical absorption correction ($T_{min} = 0.23$, $T_{max} = 0.43$), Nonius KappaCCD diffractometer, $2.93 < \theta < 33.13$, extinction coefficient = 0.031(2), 33323 measured reflections, 10270 independent reflections, 8045 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.043 [I > 2\sigma(I)]$, $wR_2 = 0.112$, 327 parameters, H atoms riding, $S = 0.986$, residual electron density +1.7 / -3.1 e \AA^{-3} .

X-ray Crystal Structure Analysis of Compound 14 (CCDC 670969): C₁₀H₁₃NO₂, $M_r = 179.21 \text{ g} \cdot \text{mol}^{-1}$, yellow plate, crystal size 0.36 x 0.14 x 0.06 mm, orthorhombic, space group $Pca2_1$, $a = 16.909(2) \text{ \AA}$, $b = 6.6595(9) \text{ \AA}$, $c = 8.3993(12) \text{ \AA}$, $V = 945.8(2) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 4$, $D_{calc} = 1.259 \text{ g} \cdot \text{cm}^3$, $\lambda = 1.54178 \text{ \AA}$, $\mu(\text{Cu-K}\alpha) = 0.714 \text{ mm}^{-1}$, Semi-empirical absorption correction ($T_{min} = 0.64$, $T_{max} = 0.75$), Bruker AXS Proteum X8 diffractometer, $5.23 < \theta < 54.15$, 16503 measured reflections, 1127 independent reflections, 1077 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.039 [I > 2\sigma(I)]$, $wR_2 = 0.106$, 119 parameters, H atoms riding, $S = 1.127$,

residual electron density +0.2 / -0.2 e Å⁻³.

X-ray Crystal Structure Analysis of Complex 19 (CCDC 670973): C₂₉H₃₉AuF₆N₄P Sb, $M_r = 907.33$ g · mol⁻¹, colorless plate, crystal size 0.20 x 0.10 x 0.04 mm, monoclinic, space group $P2_1/c$, $a = 10.2249(2)$ Å, $b = 12.4927(2)$ Å, $c = 25.8391(5)$ Å, $\beta = 100.5430(10)^\circ$, $V = 3244.88(10)$ Å³, $T = 100$ K, $Z = 4$, $D_{calc} = 1.857$ g · cm³, $\lambda = 0.71073$ Å, $\mu(Mo-K\alpha) = 5.458$ mm⁻¹, empirical absorption correction ($T_{min} = 0.20$, $T_{max} = 0.70$), Nonius KappaCCD diffractometer, $2.29 < \theta < 30.45$, 78814 measured reflections, 9813 independent reflections, 8535 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_I = 0.028$ [$I > 2\sigma(I)$], $wR_2 = 0.093$, 387 parameters, H atoms riding, $S = 1.249$, residual electron density +1.4 / -1.7 e Å⁻³.