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Mononuclear Complexes of Platinum Group Metals Containing η^6- and η^5-Cyclic Π-Perimeter Hydrocarbon and Pyridylpyrazolyl Derivatives: Syntheses and Structural Studies

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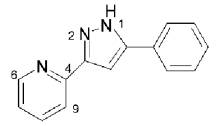
Abstract. Piano-stool-shaped platinum group metal compounds, stable in the solid state and in solution, which are based on 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**) with the formulas $[(\eta^6\text{-arene})Ru(\mathbf{L})Cl]PF_6$ {arene = C_6H_6 (**1**), *p*-cymene (**2**), and C_6Me_6, (**3**)}, $[(\eta^6\text{-}C_5Me_5)M(\mathbf{L})Cl]PF_6$ {*M* = Rh (**4**), Ir (**5**)}, and $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(\mathbf{L})]PF_6$ (**6**), $[(\eta^5\text{-}C_5H_5)Os(PPh_3)(\mathbf{L})]PF_6$ (**7**), $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(\mathbf{L})]PF_6$ (**8**), and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(\mathbf{L})]PF_6$ (**9**) were prepared by a general method and characterized by NMR and IR spectroscopy and mass spectrometry. The molecular structures of compounds **4** and **5** were established by single-crystal X-ray diffraction. In each compound the metal is connected to N1 and N11 in a k^2 manner.

1. Introduction

Mononuclear compounds of platinum group metals containing nitrogen based ligands received considerable attention because of their photochemical properties [1–9], their catalytic activities [10–19], and their electrochemical behavior [20–26], as well as in the development of new biological active agents [27–33]. In particular, η^6-arene metal complexes emerged as versatile intermediates in organic synthesis; they contain three labile coordination sites, whereas another three coordination sites are occupied by a rigid arene ring [34, 35]. They have found application in catalysis, supramolecular assemblies, and in molecular devices. Additionally, η^6-arene metal complexes showed antiviral, antibiotic, and anticancer activities. Half-sandwich complexes attracted attention because they proved to be extremely useful in stoichiometric and catalytic asymmetric syntheses [36–39]. The tetracoordinate, pseudo-tetrahedral arrangement makes them particularly suitable for investigation of the stereochemistry of reactions at the metal atom [40]. In recent years, we carried out reactions of η^5- and η^6- cyclic Π-perimeter hydrocarbon metal complexes with a variety of nitrogen-based ligands [41–48] including various polypyridyl ligands. Ruthenium compounds with these types of ligands have the capacity to function as catalysts for the oxidation of water to dioxygen [49, 50]. Although extensive studies were carried out on η^5- and η^6-transition metal complexes; compounds containing phenylpyrazolylpyridine ligands of the type shown below have not been investigated yet.



2-(5-phenyl-1H-pyrazol-3-yl)-pyridine (**L**)

Herein we describe the syntheses of nine mononuclear η^5- and η^6-cyclic Π-perimeter hydrocarbon platinum group metal compounds bearing the ligand phenylpyrazolylpyridine. Our main goal in choosing this phenyl-substituted ligand was to synthesize a series of mononuclear and dinuclear compounds by activating the carbon atom of the phenyl ring. But attempts to prepare a dimetallic derivative through the addition of a second organometallic anion by activation of the carbon atom were unsuccessful and we ended up with a series of mononuclear compounds only with metal bound to two nitrogen atoms (N1 and N11) of the ligand. All these compounds were fully characterized by IR and NMR spectroscopy, and mass spectrometry. Molecular structures of the two representative compounds are also presented in this paper.

2. Experimental Section

All solvents were dried and distilled prior to use. The ligand **L** was synthesized by following a literature method [51]. The precursor complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = C_6H_6, $C_{10}H_{14}$, and C_6Me_6), $[(\eta^6\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (*M* = Rh, Ir) [52–55], $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$, $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Br]$, $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$, and $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ were prepared by following the literature methods [56–61]. NMR spectra were recorded with a Bruker AMX 400 MHz spectrometer.

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Infrared spectra were recorded as KBr pellets with a Perkin–Elmer 983 spectrophotometer. Mass spectra were obtained with a ZQ mass spectrometer by the ESI method.

2.1. Single-Crystal X-ray Structures Analyses

Crystals of compound **4** were grown from acetone/hexane as small red plates. Crystals of compound **5** were grown by slow evaporation of a methanol solution of the respective compound as deep red blocks. The crystallizations were carried out at room temperature. The intensity data of **4** and **5** were collected with a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube Mo-K_α radiation (α = 0.71073 Å) at 273(3) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s per frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with the SAINT and XPREP software. Multi-scan empirical absorption corrections were applied to the data using the program SADABS. Structures were solved by direct methods using SHELXS-97 [62] and refined with full-matrix least-squares on F^2 using SHELXL-97 [63]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference Fourier maps and refined. Structural illustrations have been drawn with ORTEP-3 [64] for Windows. The ORTEP presentations of the representative compounds are shown in Figure 1 and Figure 2 respectively. The data collection parameters and bond lengths and angles are presented in Table 1 and Table 2.

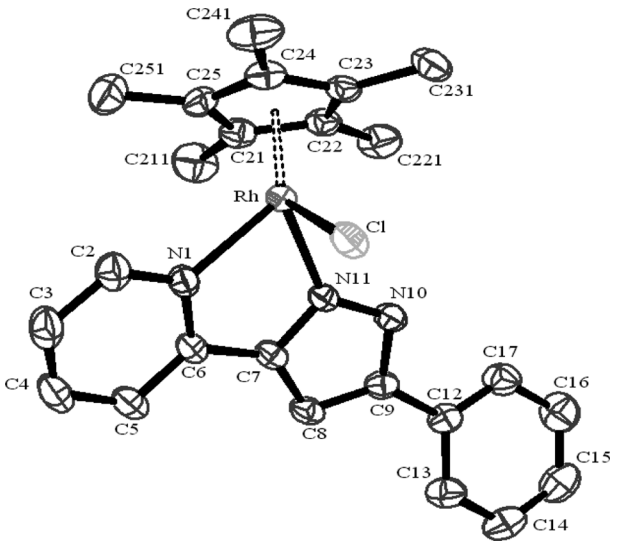

Figure 1. Molecular structure of compound **4** with 35 % probability thermal ellipsoids. Hydrogen atoms and the BF_4 ion are omitted for clarity.

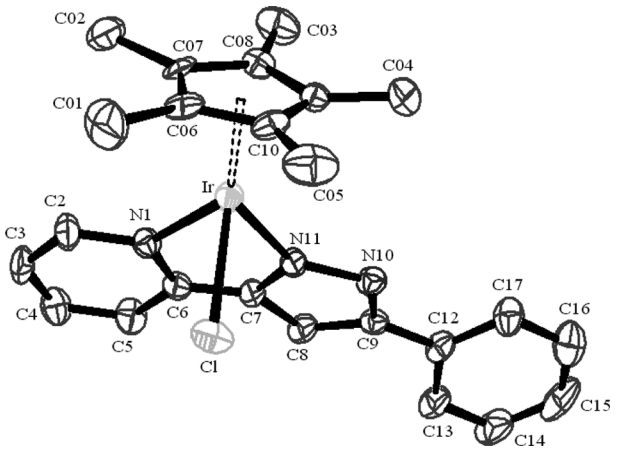

Figure 2. Molecular structure of compound **5** with 35 % probability thermal ellipsoids. Hydrogen atoms and the perchlorate ion are omitted for clarity.

CCDC-749569 (**4**) and CCDC-749570 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by E-Mail: data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033.

2.2. Syntheses

[(η^6-C_6H_6)Ru(L)Cl]PF_6 (1): A mixture of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ (100 mg, 0.2 mmol), 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**) (90 mg, 0.4 mmol), and two equivalents of NH_4PF_6 was stirred in dry methanol (30 mL) for 4 h at room temperature. The brown compound that formed was filtered, washed with ethanol and diethyl ether and dried in vacuo. Yield 90 mg, 77 %. $C_{20}H_{17}ClN_3PF_6Ru$: calcd. C 41.34; H 2.97; N 7.25 %; found: C 41.45; H 3.07; N 7.14 %. **IR** (KBr): $\tilde{\nu}$ = 3436 (ν_{N-H}); 1625 ($\nu_{C=C}$); 1457 ($\nu_{C=N}$); 846 (ν_{P-F}) cm^{-1}. **^{1}H NMR** (400 MHz, CD_3CN): δ = 9.341 (d, J = 5.6 Hz, 1 H), 8.132 (dt, J = 8.4 Hz, 3 H), 8.00 (dd, J = 8 Hz, 2 H), 7.882 (d, J = 7.2 Hz, 2 H), 7.600–7.530 (m, 1 H), 7.321 (s, 1 H), 6.079 (s, 6 H, C_6H_6). **ESI-MS** (m/z): 436.1 [M – PF_6], 400.2[M – PF_6 – Cl].

[(η^6-p-*i*PrC_6H_4Me)Ru(L)Cl]PF_6 (2): A mixture of [(η^6-$C_{10}H_{14}$)Ru(μ-Cl)Cl]$_2$ (100 mg, 0.163 mmol), 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**) (72 mg, 0.325 mmol), and two equivalents of NH_4PF_6 was stirred in dry methanol (30 mL) for 4 h at room temperature. The yellow compound that formed was filtered, washed with ethanol and diethyl ether and dried in vacuo. Yield 87 mg, 84 %. $C_{24}H_{25}ClN_3PF_6Ru$: calcd. C 45.23; H 3.99; N 6.63 %; found: C 45.33; H 3.84; N 6.48 %. **IR** (KBr): $\tilde{\nu}$ = 3446 (ν_{N-H}); 1635 ($\nu_{C=C}$); 1451 ($\nu_{C=N}$); 849 (ν_{P-F}) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.204 (d, J = 5.6 Hz, 1 H), 8.006 (t, J = 8.8 Hz, 2 H), 7.827 (t, J = 7.2 Hz, 1 H), 7.550- 7.491 (m, 1 H), 7.473 (d, J = 6.8 Hz, 2 H), 6.984 (s, 1 H), 6.341(d, J = 6 Hz, 2 H), 5.941(d, J = 6 Hz, 1 H, Ar_{p-cy}), 5.868 (d, J = 6 Hz, 1 H, Ar_{p-cy}), 5.769 (d, J = 6 Hz, 1 H, Ar_{p-cy}), 5.651(d, J = 6 Hz, 1 H, Ar_{p-cy}), 2.792 (sep, 1 H), 2.234 (s, 3 H), 1.055 (dd, J = 6.8 Hz, 6 H). **ESI-MS** (m/z): 492.1 [M – PF_6], 456.3 [M – PF_6 – Cl], 458.3 [M – PF_6 – Cl]$^{2+}$.

[(η^6-C_6Me_6)Ru(L)Cl]PF_6 (3): A mixture of [(η^6-C_6Me_6)Ru(μ-Cl)Cl]$_2$ (100 mg, 0.15 mmol), 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**) (66 mg, 0.30 mmol), and two equivalents of NH_4PF_6 was stirred in dry methanol (30 mL) for 4 h at room temperature. The solvent was removed by using a rotary evaporator. The solid was dissolved in dichloromethane and afterwards filtered to remove ammonium chloride. The solution was concentrated to 2 mL and excess of diethyl ether was added for precipitation. The light brown colored product was separated, washed with diethyl ether and dried in vacuo. Yield 84 mg, 84 %. $C_{26}H_{29}ClN_3PF_6Ru$: calcd. C 46.93; H 4.45; N 6.30 %; found: C 46.26; H 4.51; N 6.21 %. **IR** (KBr): $\tilde{\nu}$ = 3430 (ν_{N-H}); 1632 ($\nu_{C=C}$); 1452 ($\nu_{C=N}$); 847 (ν_{P-F})m cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.432 (d, J = 6.8 Hz, 1 H), 8.332 (dt, J = 8 Hz, 3 H), 8.110 (dd, J = 7.2 Hz, 2 H), 7.972 (d, J = 7.6 Hz, 2 H), 7.720–7.610 (m, 1 H), 7.431 (s, 1 H), 2.188 (s, 18 H, C_6Me_6). **ESI-MS** (m/z): 448.1 [M – PF_6], 413 [M – PF_6 – Cl].

Table 1. Crystallographic and structure refinement parameters for compounds **4** and **5**.

	4	**5**
Emperical formula	$C_{24}H_{26}BClF_4N_3Rh$	$C_{25}H_{29}Cl_2IrN_3O_5$
Formula weight	581.65	714.61
Temperature /K	293(2)	293(2)
Wavelength /Å	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P21/n$
Unit cell dimensions		
a /Å	10.5688(6)	13.0524(8)
b /Å	11.4582(7)	10.0571(9)
c /Å	11.4748(7)	20.7255(14)
α /°	116.3150(10)	90
β /°	94.7380(10)	100.251(5)
γ /°	94.3690(10)	90
Volume /A^3	1231.40(13)	2677.2(3)
Z	2	4
Calculated density /Mg·m^{-3}	1.569	1.775
Absorption coefficient /mm^{-1}	0.850	5.227
F(000)	588	1404
Crystal size /mm	0.20 × 0.10 × 0.02	0.11 × 0.08 × 0.02
Θ range for data collection /°	1.95 to 25.00	1.72 to 25.37
Index ranges	$-12 \le h \le 12$	$-14 \le h \le 14$
	$-13 \le k \le 13$	$-12 \le k \le 11$
	$-13 \le l \le 13$	$-24 \le l \le 24$
Reflections collected / unique, R_{int}	9432/4327, 0.0305	22770/4556, 0.0609
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0471$, $wR_2 = 0.1049$	$R_1 = 0.0272$, $wR_2 = 0.0316$
R indices (all data)	$R_1 = 0.0657$, $wR_2 = 0.1120$	$R_1 = 0.0790$, $wR_2 = 0.0358$
Largest diff. peak and hole /e·Å^{-3}	0.761 and –0.643	0.704 and –0.890

Table 2. Selected bond lengths and angles for compounds **4** and **5**.

	4	**5**
N(1)–M(1)	2.139(9)	2.125(3)
N(11)–M(1)	2.090(9)	2.069(2)
N(10)–N(11)	1.378(14)	1.373(3)
Cl(1)–M(1)	2.401(4)	2.399(15)
M(1)–CNT(1)[a)]	1.773	1.791
N(1)–M(1)–N(11)	75.8(4)	75.49(9)
N(10)–N(11)–M(1)	134.0(7)	133.52(17)
N(1)–M(1)–Cl(1)	85.5(3)	86.11(9)
N(11)–M(1)–Cl(1)	88.7(3)	86.74(10)

a) CNT = Metal to centroid of Cp*.

[(η^5-C_5Me_5)M(L)Cl]X {M = Rh, X = BF_4 (4), Ir, X = ClO_4 (5)}: A mixture of [(η^5-C_5Me_5)M(μ-Cl)Cl]$_2$ (M = Rh, Ir) (0.16 mmol), 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**) (71 mg, 0.32 mmol), and two equivalents of NH_4BF_4 (compound **4**) and $NaClO_4$ (compound **5**) in dry methanol (30 mL) was stirred at room temperature for 6 h until the color of the solution changed to dark yellow. The solvent was removed by using a rotary evaporator under reduced pressure. The residue was dissolved in dichloromethane (5 mL), and the solution was filtered to remove ammonium chloride. The light red solution was concentrated to 2 mL; addition of excess hexane gave the orange-yellow complex, which was separated and dried in vacuo. **Compound (4):** Yield 80 mg, 85 %. $C_{24}H_{26}ClN_3BF_4Rh$: calcd. C 49.58; H 4.57; N 7.24 %; found: C 49.67; H 4.63; N 7.13 %. **IR** (KBr): $\tilde{\nu}$ = 3438 (ν_{N-H}); 1628 ($\nu_{C=C}$); 1450 ($\nu_{C=N}$); 1088 (ν_{B-F}) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.708 (d, J = 5.6 Hz, 1 H), 8.062 (t, J = 7.6 Hz, 1 H), 7.973 (d, J = 7.6 Hz, 2 H), 7.713(d, J = 7.2 Hz, 2 H), 7.587 (t, J = 6.8 Hz, 2 H), 7.474–7.403 (m, 1 H), 7.194 (s, 1 H), 1.688 (s, 15 H, C_5Me_5). **ESI-MS** (m/z): 459.2 [M – BF_4 – Cl], 458.3 [M – BF_4 – Cl – H]. **Compound (5):** Yield 69 mg, 82 %. $C_{24}H_{26}ClN_3BF_4Ir$: calcd. C 42.99; H 3.95; N 5.53 %; found: C 43.07; H 4.04; N 5.46 %. **IR** (KBr): $\tilde{\nu}$ = 3460 (ν_{N-H}); 1634 ($\nu_{C=C}$); 1453 ($\nu_{C=N}$); 1099 (ν_{Cl-O}) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.778 (d, J = 5.6 Hz, 1 H), 8.137 (dt, J = 7.6 Hz, 2 H), 8.068 (d, J = 7.6 Hz, 2 H), 7.792 (dd, J = 6 Hz, 2 H), 7.681 (dt, J = 6.4 Hz, 1 H), 7.568–7.505 (m, 1 H), 7.383 (s, 1 H), 1.724 (s, 15 H, C_5Me_5). **ESI-MS** (m/z): 494.4 [M – BF_4], 459.1 [M – BF_4 – Cl].

[(η^5-C_5H_5)M(L)(PPh_3)]PF_6 {M = Ru (6), Os (7)}: A mixture of [(η^5-C_5H_5)M(PPh_3)$_2X$] {M = Ru, X = Cl and M = Os, X = Br} (0.137 mmol), 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**) (30 mg, 0.137 mmol), and one equivalent of NH_4PF_6 in dry methanol (30 mL) was heated under reflux for 12 h until the color of the solution changed from pale yellow to orange. The solvent was removed under vacuum, the residue was dissolved in dichloromethane (10 mL), and the solution was filtered to remove ammonium halide. The orange solution was concentrated to 5 mL. Afterwards, addition of ethyl ether gave a orange-yellow precipitate, which was separated and dried in vacuo. **Compound (6):** Yield 74 mg, 68 %. Elemental Anal (%) $C_{37}H_{31}N_3P_2F_6Ru$: calcd. C 55.94; H 3.97; N 5.27 %; found: C 56.19; H 4.08; N 5.18 %. **IR** (KBr): $\tilde{\nu}$ = 3430 (ν_{N-H}); 1628 ($\nu_{C=C}$); 1450 ($\nu_{C=N}$); 849 (ν_{P-F}) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.006 (d, J = 5.2 Hz, 1 H), 8.614 (d, J = 4.4 Hz, 2 H), 8.009 (d, J = 7.2 Hz, 2 H), 7.939 (t, J = 8 Hz, 2 H), 7.672 (t, J = 7.6 Hz, 1 H), 7.591–7.523 (m, 1 H), 7.333–7.022 (m, 15 H, PPh_3), 7.189 (s, 1 H), 4.723 (s, 5 H, C_5H_5). **^{31}P{^{1}H} NMR** ($CDCl_3$): δ = 50.82 (s, PPh_3). **ESI-MS** (m/z): 583.6 [M – PF_6], 548.2 [M – PF_6 – Cl]. **Compound (7):** Yield 75 mg, 69 %. Elemental Anal (%) $C_{35}H_{30}N_6P_2F_6Os$: calcd. C 50.31; H 3.55; N 4.72 %; found: C 50.42; H 3.63; N 4.66 %. **IR** (KBr): $\tilde{\nu}$ = 3448 (ν_{N-H}); 1629 ($\nu_{C=C}$); 1451 ($\nu_{C=N}$); 844 (ν_{P-F}) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 12.882 (s, NH, 1 H), 9.130 (d, J = 5.6 Hz, 1 H), 8.622 (d, J = 7.2 Hz, 2 H), 7.804 (d, J = 7.2 Hz, 2 H), 7.720

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(t, J = 8 Hz, 3 H), 7.573–7.498 (m, 1 H), 7.387–7.018 (m, 15 H, PPh_3), 6.560 (s, 1 H), 4.658 (s, 5 H, C_5H_5). **$^{31}P\{^1H\}$ NMR** ($CDCl_3$): δ = –0.254 (s, PPh_3). **ESI-MS** (m/z): 740.5 [M – PF_6], 738.3 [M – PF_6 – 2H], 737.3 [M – PF_6 – 3H].

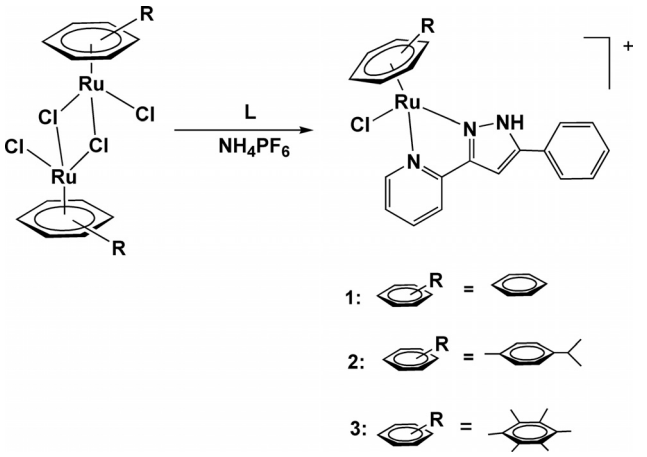
[(η^5-C_5Me_5)Ru(L)(PPh_3)]PF_6 (8): A mixture of [(η^5-C_5Me_5)Ru(PPh_3)$_2$Cl] (100 mg, 0.125 mmol), 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**) (37.7 mg, 0.125 mmol), and one equivalent of NH_4PF_6 in dry methanol (30 mL) was heated under reflux for 12 h until the color of the solution changed from pale yellow to orange. The solvent was removed by using a rotary evaporator under reduced pressure. The residue was dissolved in dichloromethane (10 mL), and the solution was filtered to remove ammonium chloride. The orange solution was concentrated to 5 mL. Addition of excess hexane gave the orange-yellow compound, which was separated and dried in vacuo. Yield 72 mg, 66 %. Elemental Anal (%) $C_{42}H_{41}N_3P_2F_6Ru$: calcd. C 58.36; H 4.80; N 4.89 %; found: C 58.43; H 4.91; N 4.76 %. **IR** (KBr): $\tilde{\nu}$ = 3434 (ν_{N-H}); 1626 ($\nu_{C=C}$); 1445 ($\nu_{C=N}$); 847 (ν_{P-F}) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.807 (d, J = 5.6 Hz, 1 H), 8.693 (d, J = 7.2 Hz, 2 H), 7.862 (t, J = 7.6 Hz, 1 H), 7.815 (t, J = 7.6 Hz, 2 H), 7.576–7.454 (m, 1 H), 7.371–7.263 (m, 15 H, PPh_3), 7.002 (d, J = 10.8 Hz, 2 H), 6.583 (s, 1 H), 2.071 (s, 15 H, C_5Me_5). **$^{31}P\{^1H\}$ NMR** ($CDCl_3$): δ = 50.430 (s, PPh_3). **ESI-MS** (m/z): 719.3[M – PF_6], 457.3 [M – PF_6 – PPh_3].

[(η^5-C_9H_7)Ru(L)(PPh_3)]PF_6 (9): A mixture of [(η^5-C_9H_7)Ru(PPh_3)$_2$Cl] (100 mg, 0.128 mmol), 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**) (38.4 mg, 0.128 mmol), and one equivalent of NH_4PF_6 in dry methanol (30 mL) was heated under reflux for 8 h until the color of the solution changed from pale yellow to dark red. The solvent was removed under vacuum. The residue was dissolved in dichloromethane (10 mL), and the solution was filtered to remove ammonium chloride. The red solution was concentrated to 5 mL. Afterwards, addition of ethyl ether gave the orange-red precipitate, which was separated and dried in vacuo. Yield 77 mg, 61 %. Elemental Anal $C_{41}H_{33}N_3P_2F_6Ru$: calcd. C 58.33; H 3.97; N 4.00 %; found: C 58.42; H 4.08; N 3.89 %. **IR** (KBr): $\tilde{\nu}$ = 3432 (ν_{N-H}); 1630 ($\nu_{C=C}$); 1453 ($\nu_{C=N}$); 847 (ν_{P-F}) cm^{-1}. **^{1}H NMR** (400MHz, $CDCl_3$): δ = 11.924 (s, NH, 1 H), 9.296 (d, J = 5.2 Hz, 1 H), 8.453 (d, J = 7.2 Hz, 2 H), 7.720 (d, J = 7.6 Hz, 2 H), 7.575 (t, J = 8 Hz, 2 H), 7.480 (t, J = 7.2 Hz, 1 H), 7.389–7.027 (m, 23 H), 6.433 (s, 1 H), 4.859 (d, J = 8 Hz, 1 H), 4.320 (t, J = 2.4 Hz, 1 H), 3.507 (dd, J = 7.2 Hz, 1 H). **$^{31}P\{^1H\}$ NMR** ($CDCl_3$): δ = 59.441 (s, PPh_3). **ESI-MS** (m/z): 20.5 [M – PF_6], 718.4 [M – PF_6 – 2H], 458.2 [M – PF_6 – PPh_3].

3. Results and Discussion

3.1. Arene Ruthenium Compounds 1–3

The dinuclear arene ruthenium complexes [(η^6-arene)Ru(μ-Cl)Cl]$_2$ (arene = C_6H_6, *p*-cymene, and C_6Me_6) react with the N,N'-based ligand (**L**) in methanol to produce the mononuclear cationic compounds **1**, **2**, and **3** (Scheme 1). Compound **1** is brown, whereas compounds **2** and **3** are yellow. The compounds are non-hygroscopic and stable in air as well as in solution. They are sparingly soluble in polar solvents like dichloromethane, chloroform, acetone, and acetonitrile but are insoluble in non-polar solvents like hexane, diethyl ether, and petroleum ether. All compounds were isolated as their hexafluorophosphate salts.



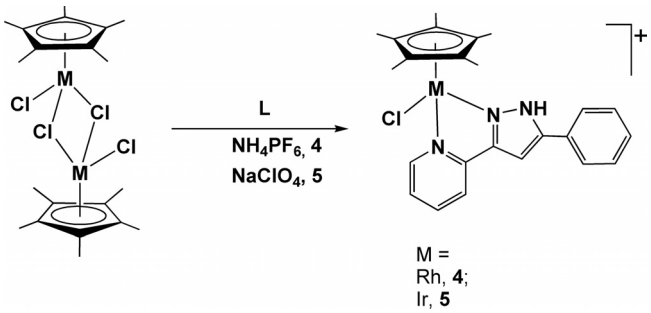
Scheme 1.

The infrared spectra of compounds **1**–**3** exhibit the signals of the chelating N,N'-bidentate ligand as broad bands at 3436, 3446, 3430, 1625, 1635, 1632, 1457, 1451, and 1452 cm^{-1}, which correspond to the stretching frequencies of the N–H bond of pyrazole ring, and of the C=C and C=N bonds of the pyridine ring of the ligand, respectively. In addition, the IR spectra of all these compounds display a strong band at about 846 cm^{-1} corresponding to the stretching frequency of the P–F bond of the counterion of these compounds. The ^{1}H NMR spectrum of the free ligand shows seven different sets of signals in the aromatic region. In the ^{1}H NMR spectra of complexes with the ligand **L,** the signals are spread over a wide range compared to the spectrum of the free ligand. Compounds **1** and **3** show a doublet signal at around 9.204 and 9.341 ppm, which corresponds to the pyridyl proton adjacent to the nitrogen atom (i.e., H6), whereas in the case of the free ligand, the same proton comes in the up-field region at around 8.601 ppm. The free ligand also shows two doublet signals in the range of 7.800–7.704 ppm, two triplet signals at around 7.426–7.261 ppm, and a multiplet and a singlet signal corresponding to the protons of the pyridyl and phenyl group of the ligand. Compound **1** exhibits a doubly triplet instead of two triplet signals corresponding to the pyridyl protons of the ligand, which is shifted downfield compared to the free ligand. In addition to all these peaks, the ^{1}H NMR spectrum of compound **1** also shows a singlet signal at around 6.079 ppm, which corresponds to the six protons of the benzene ring, whereas compound **3** exhibits a singlet signal at around 2.188 ppm corresponding to the eighteen protons of the hexamethylbenzene ring. Compound **2** exhibits an unusual pattern of resonances for the *p*-cymene ligand. For instance, the methyl protons of the isopropyl group display a doubly doublet at ca. 1.055 ppm instead of the doublet found in the starting precursor. The aromatic protons of the *p*-cymene ligand for these compounds also display four doublets at ca. 5.941–5.651 ppm, instead of two doublet signals found in the starting precursor. This pattern is due to the diastereotopic nature of the methyl protons of the isopropyl group and the aromatic protons of the *p*-cymene ligand. It may also be attributed to the behavior of the ruthenium

atom which is stereogenic when coordinated with four different ligand atoms [65]. In other words, it is obvious that the different signals are entirely due to the chiral nature of the metal [66, 67] (Scheme 1).

3.2. Pentamethylcyclopentadienyl Rhodium and Iridium Compounds 4 and 5

The dinuclear complexes $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh or Ir) undergo a bridge cleavage reaction with the N,N'-bidentate nitrogen base ligand (**L**) in methanol at room temperature, which leads to the formation of chloride-substituted compounds **4** and **5**, respectively (Scheme 2).



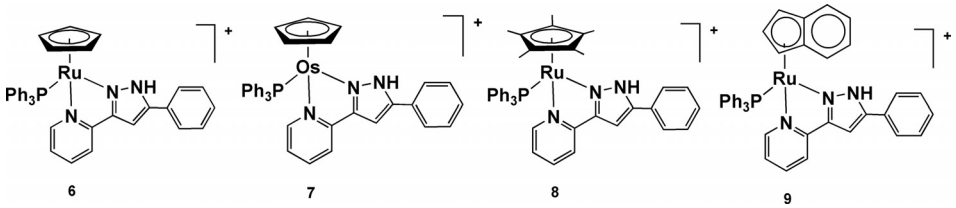
Scheme 2.

Compound **4** was isolated as its tetrafluoroborate salt, whereas compound **5** was isolated as perchlorate salt. Both compounds are orange-yellow in color and are stable in the solid state as well as in solution. They are soluble in polar solvents but insoluble in non-polar solvents like hexane, petroleum ether, and diethyl ether. The infrared spectra of both compounds exhibit the signal of the chelating N,N'-bidentate ligand as broad bands at 3438, 3460, 1628, 1634, 1450, and 1453 cm^{-1}, which correspond to the stretching frequencies of the N–H bond of the pyrazole ring and of the C=C and C–N bonds of the pyridine ring of the ligand respectively. The IR spectrum of compound **4** also exhibits a strong band at 1088 cm^{-1} due to the stretching frequency of the B–F bond of its counterion. However, in the case of compound **5**, a strong signal at 1099 cm^{-1} is observed due to the perchlorate ion [68]. Compounds **4** and **5** also show a slight downfield shift in the ^{1}H NMR spectrum compared to that of the free ligand. It shows a doublet signal at around 8.7 ppm corresponding to the proton next to the nitrogen atom of the pyridyl group of the ligand (i.e., H6) whereas in the case of the free ligand, the same proton comes at around 8.6 ppm. The spectrum of compound **5** also displays two triplet signals corresponding to the pyridyl protons at around 8.1 and 7.6 ppm, whereas the spectrum of the free ligand shows two triplet signals at around 7.4 and 7.3 ppm. Besides these signals, the other ligand signals are mentioned in the Experimental Section. The ^{1}H NMR spectra of these compounds also display a singlet signal at 1.688 ppm for compound **4** and at 1.724 ppm for compound **5** respectively, which corresponds to the protons of the pentamethylcyclopentadienyl group. The molecular structures of compounds **4** and **5** were solved by single-crystal X-ray crystallography and the structures are presented in Figure 1 and Figure 2.

3.3. Cyclopentadienyl Ruthenium and Osmium Compounds 6–9

The analytical data of these compounds are in agreement with the formulations given in Scheme 3. These mononuclear compounds are formed by the reaction of metal complexes with the ligand **L**. All complexes are isolated as their hexafluorophosphate salt. The infrared spectra of the complexes exhibit the signals of the chelating N,N'-bidentate ligand as broad bands between 3430 and 3448 cm^{-1}, 1626 and 1630 cm^{-1} and between 1445 and 1453 cm^{-1} as mentioned in the Experimental Section, which correspond to the stretching frequencies of the N–H bond of the pyrazole ring and of the C=C and C–N bonds of the pyridine ring of the ligand, respectively. In addition, the infrared spectra of these compounds also exhibit a strong band between 844 cm^{-1} and 849 cm^{-1}due to the stretching frequency of the P–F bond of the counterion. The ^{1}H spectra of compounds **6** and **7** each exhibit a singlet signal at 4.723 and 4.658 ppm for the cyclopentadienyl ring protons, which indicates a downfield shift from the starting complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-}C_5H_5)Os(PPh_3)_2Cl]$ [69, 59]. The downfield shift in the position of the cyclopentadienyl protons might result from a change in the electron density on the metal atom due to chelation of the ligand **L** through two nitrogen atoms. In addition to the other ligand signals, as mentioned in the Experimental Section, a multiplet in the range 7.387–7.018 ppm, which corresponds to the phenyl protons of the triphenylphosphine group of these compounds, is observed.

The ligand 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**) reacts with pentamethylcyclopentadienyl ruthenium(II) complexes in the presence of NH_4PF_6 in methanol, to yield the mononuclear cationic compound $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(L)]PF_6$, (**8**) (Scheme 3) This orange crystalline solid is soluble in polar solvents and air stable. The infrared spectrum of complex **8**



Scheme 3.

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displays a sharp signal at 847 cm^{-1} corresponding to the stretching frequency of the P–F bond of the counterion in addition to the bands due to ligand. The ^1H NMR spectrum also displays a singlet signal at 2.071 ppm corresponding to the methyl protons of the pentamethylcyclopentadienyl ring and a multiplet signal in the range 7.371–7.263 ppm, which corresponds to the phenyl protons of triphenylphosphine. Compound **9** exhibits three characteristic sets of signals for the protons of the indenyl group. The protons of the triphenylphosphine ligand exhibit a multiplet signal at 7.389–7.027 ppm. If the ^1H NMR spectra of all these compounds are observed carefully, it is obvious that the spectra of all compounds containing ruthenium display the ligand peak shifted downfield compared to that of the rhodium, iridium, and osmium compounds. The $^{31}P\{^1H\}$ NMR spectra of compounds **6**, **8**, and **9** exhibit a single sharp signal for triphenylphosphine at 59.441–49.625 ppm respectively, whereas in the starting precursors the signals appear in the upfield region. In the case of compound **7**, the $^{31}P\{^1H\}$ NMR spectrum display a sharp singlet signal at –0.254 ppm as compared to the starting complex which shows a signal at –6.29 ppm.

The *m*/*z* values of all compounds and their stable ion peaks obtained from the ZQ mass spectra, as listed in the Experimental Section, are in good agreement with the theoretically expected values. The ESI mass spectra also displayed prominent peaks corresponding to the molecular ion fragments. All halogenated compounds displayed a prominent peak corresponding to the loss of the chloride ion from the molecular ion peak, but the loss of arene or Cp or Cp* group is not observed, which indicates that the stronger bond of the metal ions to these groups remains intact. Similarly, in some of the compounds containing the triphenylphosphine ligand, the loss of the triphenylphosphine group from the molecular ion peak is obvious, which is also given in the Experimental Section.

4. Molecular Structures

The molecular structures of **4** and **5** were determined by single-crystal X-ray diffraction. The compounds crystallize in space groups $P\bar{1}$ and $P2_1/n$. Compound **5** crystallizes with a molecule of methanol per asymmetric unit. In compound **4**, the presence of an oriental disorder for the location of the counterion BF_4 is observed. Details about data collection, refinement and structure solution are recorded in Table 1, selected bond lengths and angles are presented in Table 2. Crystal structures of compounds **4** and **5** with atom-numbering schemes are shown in Figure 1 and Figure 2. In both compounds, the metal atom is bound to the major coordinated sites N1 and N11 in a k^2 manner, and to one chloro group, and the pentamethylcyclopentadienyl (Cp*) ring in a η^5 manner. The typical piano-stool-shaped arrangement around the metal atom in both compounds is maintained. The Cp* ring is planar with average Rh–C and Ir–C distance of 2.149 and 2.159 Å, respectively. The bond length of the rhodium metal atom to the centroid (CNT) of the Cp* amounts to 1.773 Å in the case of compound **4**, whereas in the case of compound **5** the iridium atom to the centroid (CNT) of the Cp* distance amounts to 1.791 Å, which are similar to the distances in other rhodium and iridium pentamethylcyclopentadienyl compounds. The Rh–N and Rh–Cl bond lengths are in agreement with the values reported in the literature [65, 70–72]. The C–C bond lengths within the Cp* ring and C–Me distances are in the normal range. The B–F and Cl–O bond lengths are in agreement with the values reported previously [41, 43].

5. Conclusions

A series of new η^5-and η^6- cyclic Π-perimeter hydrocarbon metal compounds with the ligand 2-(5-phenyl-1H-pyrazol-3-yl)pyridine (**L**), which are remarkably stable in the solid state and in solution were synthesized in good yield. Our main goal to synthesize dimetallic compounds by incorporating a second metal coordinating through the third nitrogen atom and activating the carbon atom of the phenyl group of ligand **L** was not successful.

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