Hetero-binuclear complexes containing a Ru^0 → M^{n+} bond bridged by P,N-phosphine ligands: convenient synthesis of tridentate organometallic *trans*-Ru(CO)$_3$(L)$_2$ (L = phosphine bearing an N-donor substituent) ligands

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A convenient new synthesis of *trans*-Ru(CO)$_3$(μ-L)$_2$ [L = 2-(diphenylphosphino)pyridine, *N*-(diphenylphosphinomethyl)morpholine)] was developed. The reactions of these two tridentate organometallic ligands with selected group 11 and 12 metal salts resulted in the formation of hetero-binuclear Ru^0 → M^{n+} [M = Ag(I), *n* = 1; Hg(II), Cd(II), *n* = 2] complexes with Ru–Ag = 2.7132(7) Å, Ru–Hg = 2.7075(4) Å and Ru–Cd = 2.7750(9) Å, as determined by X-ray crystallography.

Binuclear complexes containing a metal–metal bond have been studied intensively due to their interesting structural features, spectral properties and wide applications.[1] The formation of a metal–metal bond depends on two factors: (i) a favorable Lewis acid-base relationship between the two metals and (ii) suitability of the bridging ligands. Most binuclear complexes are stabilized through a bridging ligand with short dentate separation, but unsupported metal–metal dative bonds can also be formed.[2] The hemilabile bridging ligand 2-(diphenylphosphino)pyridine, Ph$_2$Ppy, has been widely used to coordinate different metals.[3] Due to the presence of its basic nitrogen site that acts as an effective "proton messenger", the monodentate P-coordination mode of Ph$_2$Ppy plays a crucial role in the rhodium-catalyzed hydroformylation of styrene and palladium-catalyzed carbonylation of alkynes.[3e–g] On the other hand, due to electronic differentiation between the nitrogen and phosphorus sites, this ligand readily coordinates different metals to form hetero-binuclear complexes, some of which exhibit interesting luminescent properties.[1b,3] In some catalytic applications, the synergistic effect confers to the hetero-binuclear complexes higher activities and conversion rates as compared to the mononuclear complexes.[3]

Binuclear complexes containing a ruthenium carbonyl group and a metal–metal dative bond are scarce as there exists no efficient method of preparing mononuclear P-coordinated ruthenium(0) carbonyl compounds.[4] Here we report a new procedure to synthesize *trans*-Ru(CO)$_3$(Ph$_2$Ppy)$_2$ whose hetero-binuclear complex with silver(I) is also described.

Thus far, most *P*,*N*-phosphine ligands used in the synthesis of metal–metal bonded binuclear complexes have been rigid pyridylphosphine ligands with a short P,N-donor separation. The paucity of aminophosphine ligands functioning in the bidentate bridging mode is due to (i) the nearly planar configuration around the amino nitrogen atom in a primary amine, secondary amine or aromatic amine and (ii) the low Lewis basicity of a tertiary amine, which does not favor its coordination to a metal center. Our previous work has established that the tertiary amino nitrogen atom in a cylclohexane-like ring such as piperazine[5a] or morpholine[5b] has a pyramidal configuration that ensures its efficient coordination to a metal atom. Hence we employed the non-rigid phosphine ligand *N*-(diphenylphosphinomethyl)morpholine, Ph$_2$PCH$_2$morph, to prepare the new tridentate organometallic ligand *trans*-Ru(CO)$_3$(Ph$_2$PCH$_2$morph)$_2$, whose reactivity and formation of hetero-binuclear complexes with mercury(II) and cadmium(II) salts are also reported.

Experimental

Unless otherwise stated, all reactions were performed under a nitrogen atmosphere using Schlenk techniques. The solvents were purified by standard methods. Infrared spectra were recorded on a Shimadzu 435 spectrometer as KBr discs. The ^{31}P{^{1}H} NMR spectra were recorded on a JEOL EX270 spectrometer at 109.25 MHz using H$_3$PO$_4$ as the external standard and CDCl$_3$ as solvent. Ru$_3$(CO)$_{12}$ (Strem) was used as received, as were AgOTf (Acros), HgI$_2$ (Strem), CdI$_2$ (Strem) and Ph$_2$PH (Aldrich). The ligand 2-(diphenylphosphino)pyridine was prepared by the literature method.[3a]

Synthetic procedures

***N*-(Diphenylphosphinomethyl)morpholine.** This ligand, abbreviated as Ph$_2$PCH$_2$morph, was used in our previous work[5b] but the synthetic procedure and ^{31}P{^{1}H}NMR spectra data were not reported. Ph$_2$PH (9.3 g, 50 mmol), morpholine (4.3 g, 50 mmol) and finely ground paraformaldehyde (1.65 g, 55 mmol) were added to 100 cm^3 toluene with stirring; the mixture was heated to 70–80 °C and stirred at this temperature for 24 h to form a clear solution. After cooling, the solution was filtered through a 2 cm celite pad, and the solvent was removed from the filtrate *in vacuo*. EtOH (50 ml) was added to the oily residue and the solution was cooled to −20 °C overnight. Colorless micro-crystals of Ph$_2$PCH$_2$morph were collected by filtration in 65% yield. m.p. 53–55 C; ^{31}P{^{1}H}NMR: $\delta = -27.1$.

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***trans*-[Ru(CO)$_3$(Ph$_2$Ppy)$_2$], 1.** [4]$Ru_3(CO)_{12}$ (1 mmol) was added to a Schlenk tube containing 20 cm^3 liquid ammonia at −50 °C. Then cut pieces of sodium metal (6 mmol) were introduced and the colorless solution immediately turned blue. The solution was stirred continuously for 2 h at −50 °C, during which time the color changed to pale yellow; liquid ammonia was then allowed to slowly evaporate. After the residue was further dried in vacuum to remove the residual ammonia, a mixture of 20 cm^3 EtOH with 0.15 g (1.5 mmol) concentrated H_2SO_4 (98%) was added and the solution stirred for 2 min. The phosphine ligand Ph_2Ppy (6 mmol) was next introduced and the solution heated to 70 °C for 2 h, during which time a large amount of yellow precipitate appeared. After the reaction was complete, the solution was cooled to room temperature and the precipitate was filtered. The solid was dissolved in 20 cm^3 CH_2Cl_2, filtered, and concentrated to 5 cm^3. Then 15 cm^3 CH_3OH was added and the solution cooled in a refrigerator overnight. Pure product **1** appeared as a pale yellow precipitate and was collected by filtration and vacuum dried. Yield: 50%. The ν(CO) IR and ^{31}P NMR spectra were identical to those reported in the literature.[4] IR (νCO): 1897s cm^{-1}; $^{31}P\{^1H\}$ NMR: $\delta = 50.1$.

***trans*-[Ru(CO)$_3$(Ph$_2$PCH$_2$morph)$_2$], 2.** The above procedure was repeated using PH_2PCH_2morph to give **2** in 65% yield. Anal. found: C, 58.85; H, 5.28; N, 3.60; calcd for $C_{37}H_{40}N_2O_5P_2Ru$: C, 58.80; H, 5.33; N, 3.71. IR (νCO): 1973w, 1885s cm^{-1}; $^{31}P\{^1H\}$ NMR: $\delta = 16.8$.

[Ru(μ-Ph$_2$Ppy)$_2$(CO)$_3$AgCF$_3$SO$_3$], 3. $AgCF_3SO_3$ (0.036 g, 0.14 mmol) was added to a solution of **1** (0.1 g, 0.14 mmol) in THF (5 cm^3). The mixture was stirred for 20 min at room temperature. The solution was filtered and the filtrate concentrated. Benzene was diffused into the concentration solution to give yellow crystals of **3** (0.109 g, 80%). Anal. found: C, 47.17; H, 3.11; N, 2.93; calcd for $C_{38}H_{28}N_2O_6F_3P_2SRuAg$: C, 47.12; H, 2.91; N, 2.89. IR (νCO): 2022s, 1978s, 1951s cm^{-1}; $^{31}P\{^1H\}$ NMR: $\delta = 59.4$.

[Ru(μ-Ph$_2$PCH$_2$morph)$_2$(CO)$_3$HgI$_2$], 4. HgI_2 (0.068 g, 0.15 mmol) was added to a solution of **2** (0.1 g, 0.13 mmol) in dichloromethane (30 cm^3). The mixture was stirred for 2 h at room temperature. The solution was filtered and the filtrate concentrated. *n*-Hexane was added to deposit **4** as a yellow solid (0.13 g, 83%). Anal. found: C, 37.05; H, 3.26; N, 2.25; calcd for $C_{37}H_{40}N_2O_5P_2RuI_2Hg$: C, 36.72; H, 3.33; N, 2.31. IR (νCO): 2060m, 1999s cm^{-1}; $^{31}P\{^1H\}$ NMR: $\delta = 34.4$, $^2J(^{199}Hg, ^{31}P) = 123$ Hz. Re-crystallization of **4** in $CHCl_3$–Et_2O yielded yellow crystals of **4** · Et_2O for X-ray analysis.

[Ru(μ-Ph$_2$PCH$_2$morph)$_2$(CO)$_3$CdI$_2$], 5. CdI_2 (0.055 g, 0.15 mmol) was added to a solution of **2** (0.1 g, 0.13 mmol) in dichloromethane (15 cm^3). The mixture was stirred for 2 h at room temperature. The solution was filtered and the filtrate concentrated. Ether was added to deposit yellow crystals of **5** · Et_2O (0.095 g, 65%). Anal. found: C, 40.06; H, 3.35; N, 2.30; calcd for $C_{37}H_{40}N_2O_5P_2RuI_2Cd$: C, 39.61; H, 3.59; N, 2.50. IR (νCO): 2034m, 1983s, 1955s cm^{-1}; $^{31}P\{^1H\}$ NMR: $\delta = 36.9$, $^2J(^{111}Cd, ^{31}P) = 28$ Hz. Re-crystallization of **5** in $CHCl_3$–Et_2O yielded well-formed yellow crystals of **5** · Et_2O for X-ray analysis.

***trans,cis*-Ru(CO)$_2$(μ-Ph$_2$PCH$_2$morph)$_2$Cl$_2$, 6.** This compound can be prepared in two ways. Method a: compound **2** (0.1 g, 0.13 mmol) and $HgCl_2$ (0.035 g, 0.13 mmol) were mixed in dichloromethane (10 cm^3) and the solution was stirred for 2 h. After filtering off the black precipitate, the solution was concentrated. Et_2O diffusion gave colorless crystals of **6** · CH_2Cl_2 (0.08 g, 70%). Method b: compound **2** was dissolved in dichloromethane and the solution was allowed to stand for 1 week. Methanol was added to deposit yellow crystals of **6** · 0.5CH_2Cl_2 (0.104 g, 95%) at −20 °C. Anal found: C, 54.05; H, 4.93; N, 3.34; calcd for $C_{36}H_{40}N_2O_4Cl_2P_2Ru$: C, 54.14; H, 5.05; N, 3.51. IR (νCO): 2050s, 1987s cm^{-1}; $^{31}P\{^1H\}$ NMR: $\delta = 21.2$.

X-Ray crystallography

For complexes **3** and **4** · Et_2O, a selected single crystal was mounted on a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 30 mA using Mo-Kα radiation (0.71073 Å). Data collection at 293 K and reduction were performed using SMART and SAINT software,[6] with frames of 0.3° oscillation in the range $1.5° < \theta < 28°$. An empirical absorption correction was applied using the SADABS program.[7]

The data for **5** · Et_2O was collected at 293 K on a Rigaku RAXIS IIC imaging plate diffractometer using Mo-Kα radiation from a rotating anode generator operating at 50 kV and 90 mA, 36/5° oscillation frames in the range of 0–180°, and exposure of 8 min per frame. A self-consistent semi-empirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied using the ABSCOR program.[8]

The data for **6** · CH_2Cl_2 and **6** · 0.5CH_2Cl_2 were collected at 293 K in the variable ω-scan mode on a Siemens R3m/V four-circle diffractometer using Mo-Kα radiation (50 kV, 30 mA; $2\theta_{max} = 50°$ for **6** · CH_2Cl_2 and 52° for **6** · 0.5CH_2Cl_2). An empirical absorption correction was applied using ψ-scan data.

All structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTL package.[9] Non-hydrogen atoms were subjected to anisotropic refinement. All hydrogen atoms were generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters, and included in structure factor calculations in the final stage of F^2 refinement. Selected X-ray data are given in Table 1.

CCDC reference numbers 169883–169887. See http://www.rsc.org/suppdata/nj/b1/b108287f/ for crystallographic data in CIF or other electronic format.

Results and discussion

Over the years, the synthesis of *trans*-Ru(CO)$_3$(L)$_2$ (L = phosphine ligand) has been developed in several ways. For instance:

(i) Ligand-exchange reaction:[4b]

$$Ru_3(CO)_{12} + cod \rightarrow Ru(CO)_3(cod)$$

$$Ru(CO)_3cod + PR_3 \xrightarrow{80\ ^\circ C} trans\text{-}Ru(CO)_3(PR_3)_2$$

(ii) Redox reaction:[10a]

$$RuCl_3 + PR_3 + HCOH + KOH \xrightarrow{110-130\ ^\circ C} trans\text{-}Ru(CO)_3(PR_3)_2$$

(iii) Photochemical reaction:[4a]

$$Ru_3CO_{12} + PR_3 \xrightarrow{h\nu/r.t} trans\text{-}Ru(CO)_3(PR_3)_2$$

It is not convenient to use Ru(CO)$_3$(cod) in the synthesis because it slowly decomposes, even when stored at −20 °C.[10b,c] The second method is very useful for phosphine ligands that contain no basic and heat-sensitive functional groups, but it is not applicable if the ligand contains a N-donor atom, which would preferentially coordinate to the Ru atom at the expense

Table 1 X-ray crystallographic data refinement parameters of the complexes

	3	**4** · Et_2O	**5** · Et_2O	**6** · CH_2Cl_2	**6** · $0.5CH_2Cl_2$
Formula	$C_{38}H_{28}AgF_3N_2$-O_6P_2RuS	$C_{37}H_{40}HgI_2N_2$-$O_5P_2Ru \cdot Et_2O$	$C_{37}H_{40}CdI_2N_2$-$O_5P_2Ru \cdot Et_2O$	$C_{36}H_{40}Cl_2N_2$-$O_4P_2Ru \cdot CH_2Cl_2$	$C_{36}H_{40}Cl_2N_2$-$O_4P_2Ru \cdot 0.5CH_2Cl_2$
M	968.56	1284.23	1196.04	883.54	841.07
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Tetragonal
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$I4_1/a$ (no. 88)
a/Å	11.170(2)	14.6934(8)	14.682(3)	11.062(2)	20.928(2)
b/Å	11.430(2)	12.7794(7)	12.739(3)	11.362(2)	20.928(2)
c/Å	18.240(3)	24.918(1)	24.921(5)	18.146(4)	17.798(4)
α/°	75.620(3)	90	90	95.48(2)	90
β/°	74.322(3)	91.410(1)	91.54(3)	94.42(2)	90
γ/°	64.449(3)	90	90	113.05(1)	90
U/Å^3	1999.5(5)	4677.4(4)	4659.4(16)	2072.8(7)	7795(2)
Z	2	4	4	2	8
μ(Mo-Kα)/mm^{-1}	1.060	5.033	2.218	0.752	0.730
Total reflect.	14 093	31 692	13 197	8671	6595
Unique reflect. (R_{int})	9437 (0.0379)	11 260 (0.0403)	7730 (0.0704)	7300 (0.0538)	2914 (0.0490)
Obsd reflect.	4764	7303	6754	4132	1910
$R1$, $wR2$ [$I > 2\sigma(I)$][a]	0.0553, 0.1187	0.0311, 0.0602	0.0601, 0.1605	0.0670, 0.1238	0.0487, 0.1274
$R1$, $wR2$ (all data)	0.1287, 0.1501	0.0628, 0.0670	0.0702, 0.1688	0.1363, 0.1531	0.0893, 0.1464

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR2 = \{w[\Sigma(|F_o| - |F_c|)^2]/\Sigma|F_o|^2\}^{1/2}$.

of the desired P-coordination. The third method is a photochemical process using ultra-violet radiation, and the optimum reaction conditions change with different ligands. In cases where the phosphine ligand bears a photo-sensitive group such as anthracene, it is not workable. Clearly, there is a need for a new convenient procedure that makes use of commercially available chemicals as starting materials.

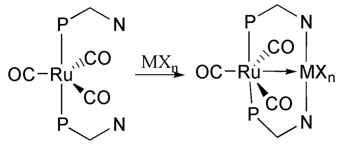
It is noted that a selective synthesis of the iron analog *trans*-$Fe(CO)_3(PR_3)_2$ was reported in the late 1980's by Keiter and Brunet and their coworkers,[11] who used $Fe(CO)_5$ to react with KOH (or NaOH, or $NaBH_4$) and different types of phosphine ligands PR_3 in refluxing *n*-butanol or ethanol to obtain the product in high yield. The key intermediate of this reaction is $[HFe(CO)_4]^-$, which suggests to us that an analogous reaction with $[HRu(CO)_4]^-$ as an intermediate might be feasible. However, unlike its iron analog $Fe(CO)_5$, $Ru(CO)_5$ is rather unstable and cannot be used as a starting material. On the other hand, it is known that $Ru_3(CO)_{12}$ reacts with a solution of sodium metal in liquid ammonia to form $Na_2[Ru(CO)_4]$.[12] Accordingly, we proceeded to carry out the reaction as represented by the following equation and obtained *trans*-$Ru(CO)_3(L)_2$ (L = P,N-phosphine ligand) in good yield:

$$Ru_3(CO)_{12} + Na(NH_3) \rightarrow Na_2[Ru(CO)_4]$$

$$\xrightarrow[\text{(ii) 2 equiv. L}]{\text{(i) 0.25 equiv. } H_2SO_4} trans\text{-}Ru(CO)_3(L)_2$$

The key intermediate $[HRu(CO)_4]^-$ is more reactive than $[HFe(CO)_4]^-$, as the reaction time of 2 h for the ruthenium complex is 12 times less than that required for the iron complex. It is worthy of note that an attempt to prepare the osmium analog using $Os_3(CO)_{12}$ by the same procedure was unsuccessful, though the reason is unclear.

The reaction of ligands **1** and **2** with different metal salts is shown in Scheme 1. Ligand **1** has been employed to react with group 12 metal salts in CH_2Cl_2 to form binuclear compounds that feature a weak Ru–Zn bond, a strong Ru–Hg bond, and strong Ru–Cd bonds.[4b] However, using copper(I) and silver(I) salts under the same conditions resulted in a redox reaction in which **1** suffered decomposition and the metal(I) ions were reduced to metallic powder. This phenomenon is similar to that observed in the reaction of $Fe(CO)_3(PR_3)_2$ with silver salts {which yield metallic silver and the unstable cationic radical $[Fe(CO)_3(PR_3)_2]^+$}[13] and indicates that the $[Ru(CO)_3(Ph_2Ppy)_2]^+$ radical is also formed. On the other hand, it has been reported that silver salts are less exoergic in THF than in CH_2Cl_2.[14] So we carried out the reaction in THF instead of CH_2Cl_2 and obtained the Ru–Ag binuclear complex, although the Ru–Cu complex proved to be unstable and was not isolated.



1 or 2 **3-5**

P⌒N = 2-(diphenylphosphino)pyridine, **1**
MX_n = $AgCF_3SO_3$, **3**
P⌒N = *N*-(diphenylphosphinomethyl)morpholine, **2**
MX_n = HgI_2, **3**
CdI_2, **4**

Scheme 1

According to our previous findings,[5b,15] when the organometallic ligand *trans*-$M(CO)_3(PR_3)_2$ coordinates with another metal to form a binuclear complex, (i) the local symmetry of M changes from D_{3h} to C_{2v}, which causes ν(CO) splitting, and (ii) the formation of a metal–metal dative bond decreases the electron density at M and consequently the $d_\pi(M) \rightarrow \pi^*(CO)$ π-back bonding, which results in an increase of ν(CO) with respect to the free ligand. As expected, the ν(CO) IR spectrum of binuclear complex **3** shows both characteristics. The ^{31}P NMR spectrum of complex **3** exhibits a singlet at 59.4 ppm, indicating that the two phosphine moieties are chemically equivalent.

The molecular structure of compound **3** is depicted in Fig. 1, and selected bond lengths and angles are listed in Table 2. Complex **3** displays a distorted octahedral geometry about the Ru atom, in which both P–Ru bonds are tilted toward the silver atom with an unusually small P(1)–Ru(1)–P(2) angle of 155.53(6)°. This is rather different from what is seen in the related binuclear complexes $Ru(CO)_3(\mu\text{-}Ph_2Ppy)_2MCl_2$ (M = Zn, Cd, Hg),[4b] in which the RuP_2 unit is much closer to being linear [P–Ru–P angle: 169.6(1)–173.9(1)°], and in the iron analogs $Fe(CO)_3(\mu\text{-}Ph_2Ppy)_2MX_2$ (M = Cu, Ag, Cd, Hg; X = Cl, Br, I, SCN, ClO_4), in which the FeP_2 unit is also close to linear (P–Fe–P angle: 168–174°). On the other hand, the three CO ligands and silver atom lie approximately in a plane. The silver atom is four-coordinated and adopts a distorted tetrahedral geometry with Ag–N = 2.373(5) and 2.404(6) Å, Ag–O = 2.295(6) Å and Ru–Ag = 2.7132(7) Å, while the bond angles vary from 93.2(1) to 144.0(2)°. The Ru–Ag distance is smaller than the sum of the metallic radii of Ru and Ag

Table 2 Selected bond lengths (Å) and angles (°) for molecules **3**–**6**

3			
Ru(1)–C(1)	1.944(8)	Ag(1)–Ru(1)	2.7132(7)
Ru(1)–C(2)	1.926(7)	Ag(1)–N(1)	2.373(5)
Ru(1)–C(3)	1.918(7)	Ag(1)–N(2)	2.404(6)
Ru(1)–P(1)	2.367(2)	Ag(1)–O(4)	2.295(6)
Ru(1)–P(2)	2.357(2)		
P(1)–Ru(1)–P(2)	155.53(6)	P(2)–Ru(1)–Ag(1)	78.10(4)
C(1)–Ru(1)–C(2)	100.1(3)	C(1)–Ru(1)–Ag(1)	72.3(2)
C(1)–Ru(1)–C(3)	156.5(3)	C(2)–Ru(1)–Ag(1)	172.4(2)
C(2)–Ru(1)–C(3)	103.4(3)	C(3)–Ru(1)–Ag(1)	84.2(2)
C(1)–Ru(1)–P(1)	89.0(2)	O(4)–Ag(1)–Ru(1)	144.0(2)
C(2)–Ru(1)–P(1)	102.0(2)	N(1)–Ag(1)–Ru(1)	93.9(1)
C(3)–Ru(1)–P(1)	86.5(2)	N(2)–Ag(1)–Ru(1)	93.2(1)
C(1)–Ru(1)–P(2)	88.0(2)	N(1)–Ag(1)–N(2)	110.3(2)
C(2)–Ru(1)–P(2)	102.4(2)	O(4)–Ag(1)–N(1)	105.4(2)
C(3)–Ru(1)–P(2)	86.6(2)	O(4)–Ag(1)–N(2)	107.6(2)
P(1)–Ru(1)–Ag(1)	77.86(4)		
4 · Et$_2$O			
Ru(1)–C(1)	1.950(4)	Ru(1)–P(2)	2.389(1)
Ru(1)–C(2)	1.938(5)	Hg(1)–Ru(1)	2.7075(4)
Ru(1)–C(3)	1.947(5)	Hg(1)–I(1)	2.8128(4)
Ru(1)–P(1)	2.387(1)	Hg(1)–I(2)	2.7948(4)
P(1)–Ru(1)–P(2)	178.83(4)	C(2)–Ru(1)–C(3)	101.3(2)
C(1)–Ru(1)–P(1)	90.2(1)	P(1)–Ru(1)–Hg(1)	86.55(3)
C(2)–Ru(1)–P(1)	89.0(1)	P(2)–Ru(1)–Hg(1)	93.37(3)
C(3)–Ru(1)–P(1)	92.0(1)	C(1)–Ru(1)–Hg(1)	81.3(1)
C(1)–Ru(1)–P(2)	88.6(1)	C(2)–Ru(1)–Hg(1)	175.1(1)
C(2)–Ru(1)–P(2)	91.1(1)	C(3)–Ru(1)–Hg(1)	76.9(1)
C(3)–Ru(1)–P(2)	89.1(1)	Ru(1)–Hg(1)–I(2)	127.74(1)
C(2)–Ru(1)–C(1)	100.6(2)	Ru(1)–Hg(1)–I(1)	122.57(1)
C(3)–Ru(1)–C(1)	158.0(2)	I(2)–Hg(1)–I(1)	106.62(1)
5 · Et$_2$O			
Ru(1)–C(1)	1.930(8)	Ru(1)–Cd(1)	2.7750(9)
Ru(1)–C(2)	1.937(7)	Cd(1)–N(1)	2.519(5)
Ru(1)–C(3)	1.941(7)	Cd(1)–I(1)	2.7728(8)
Ru(1)–P(1)	2.372(2)	Cd(1)–I(2)	2.7857(9)
Ru(1)–P(2)	2.379(2)		
P(1)–Ru(1)–P(2)	178.64(6)	C(1)–Ru(1)–Cd(1)	74.7(2)
C(1)–Ru(1)–C(2)	103.9(3)	C(2)–Ru(1)–Cd(1)	171.9(2)
C(1)–Ru(1)–C(3)	154.1(3)	C(3)–Ru(1)–Cd(1)	80.2(2)
C(2)–Ru(1)–C(3)	101.9(3)	P(1)–Ru(1)–Cd(1)	83.05(5)
C(1)–Ru(1)–P(1)	93.0(2)	P(2)–Ru(1)–Cd(1)	97.28(5)
C(2)–Ru(1)–P(1)	89.1(2)	N(1)–Cd(1)–I(1)	112.8(1)
C(3)–Ru(1)–P(1)	90.1(2)	N(1)–Cd(1)–Ru(1)	93.8(1)
C(1)–Ru(1)–P(2)	88.4(2)	I(1)–Cd(1)–Ru(1)	123.18(2)
C(2)–Ru(1)–P(2)	90.6(2)	N(1)–Cd(1)–I(2)	93.3(1)
C(3)–Ru(1)–P(2)	88.7(2)	I(1)–Cd(1)–I(2)	107.74(3)
6 · CH$_2$Cl$_2$			
Ru(1)–C(1)	1.854(9)	Ru(1)–P(2)	2.407(2)
Ru(1)–C(2)	1.894(8)	Ru(1)–Cl(1)	2.441(2)
Ru(1)–P(1)	2.411(2)	Ru(1)–Cl(2)	2.447(2)
C(1)–Ru(1)–C(2)	90.6(3)	P(1)–Ru(1)–Cl(1)	87.70(7)
C(1)–Ru(1)–P(1)	96.0(2)	P(2)–Ru(1)–Cl(1)	88.59(7)
C(2)–Ru(1)–P(1)	92.4(2)	C(1)–Ru(1)–Cl(2)	177.2(3)
C(1)–Ru(1)–P(2)	90.1(2)	C(2)–Ru(1)–Cl(2)	86.6(2)
C(2)–Ru(1)–P(2)	91.0(2)	P(1)–Ru(1)–Cl(2)	84.49(7)
P(2)–Ru(1)–P(1)	173.05(7)	P(2)–Ru(1)–Cl(2)	89.63(6)
C(1)–Ru(1)–Cl(1)	92.9(3)	Cl(1)–Ru(1)–Cl(2)	89.91(7)
C(2)–Ru(1)–Cl(1)	176.5(2)		
6 · 0.5CH$_2$Cl$_2$[a]			
Ru(1)–C(1)	1.880(9)	Ru(1)–Cl(1)	2.432(2)
Ru(1)–P(1)	2.410(1)		
C(1)–Ru(1)–C(1)#1	89.7(5)	C(1)–Ru(1)–Cl(1)	178.6(2)
C(1)–Ru(1)–P(1)	94.1(2)	P(1)–Ru(1)–Cl(1)#1	87.24(5)
C(1)–Ru(1)–P(1)#1	91.3(2)	P(1)–Ru(1)–Cl(1)	87.34(5)
P(1)#1–Ru(1)–P(1)	172.4(1)	Cl(1)#1–Ru(1)–Cl(1)	89.4(1)
C(1)–Ru(1)–Cl(1)#1	90.5(2)		

[a] Symmetry code #1: $-x + 1$, $-y + 3/2$, z.

(2.78 Å) and those in ruthenium clusters containing a Ru–Ag bond: 2.812 and 2.825 Å[16a] in Ru$_4$H$_2$(CO)$_{12}$Ag(Ph$_3$P)$_2$ · CH$_2$Cl$_2$, 2.730 and 2.802 Å[16b] in (dppm)$_2$Ru$_3$(CO)$_8$Ag(CF$_3$CO$_2$) · 0.5CH$_2$Cl$_2$, and 2.767 and 2.806 Å[16c] in (dppm)Ru$_3$(CO)$_{12}$AgPPh$_3$. This is suggestive of the presence of a fairly strong Ru → Ag donor–acceptor bond in **3**.

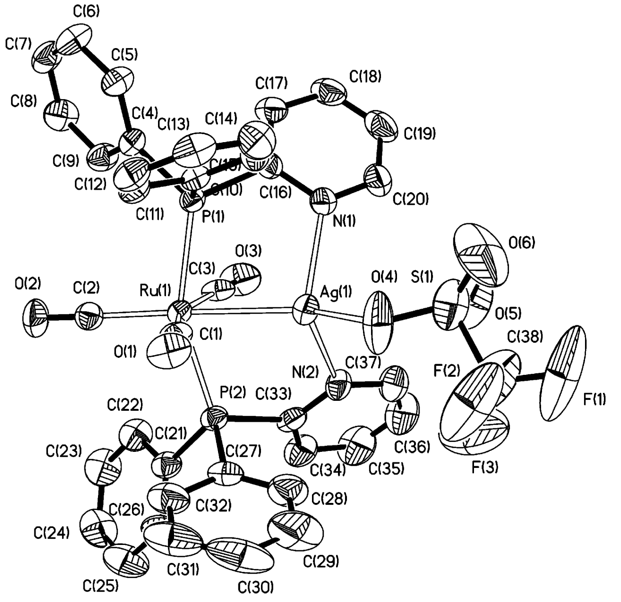


Fig. 1 Perspective view (35% thermal ellipsoids) of the molecular structure of $[Ru(CO)_3(\mu\text{-}Ph_2Ppy)_2AgCF_3SO_3]$, **3**. In this and all other figures, the hydrogen atoms have been omitted for clarity.

N-(Diphenylphosphinomethyl)morpholine, Ph_2PCH_2morph, is a non-rigid ligand whose phosphorus and nitrogen atoms are more basic than those in Ph_2Ppy. On the other hand, the basicity of Ru is higher than that of Fe.[4b] This may be the reason that Ph_2PCH_2morph reacts with $Na[RuH(CO)_4]$ to give a higher yield of compound **2** than the reaction of Ph_2Ppy. Similar to the iron analog, compound **2** exhibits a strong ν(CO) at 1885 cm^{-1}, indicating that the three CO groups are equivalent; the ^{31}P NMR signal of **2** is a singlet at 16.8 ppm, indicating that the two phosphine moieties are chemically equivalent.

Treatment of **2** with HgI_2 and CdI_2 gave the corresponding hetero-bimetallic complexes **4** and **5**, respectively. The IR spectra of **4** and **5** also show splitting and a shift to higher wavenumbers, as expected. The ^{31}P NMR spectra of compounds **4** and **5** each exhibits a singlet with two low-intensity satellite peaks $[^2J(^{199}Hg, ^{31}P) = 123$ Hz and $^2J(^{111}Cd, ^{31}P) = 28$ Hz]. The coupling values are comparable with those in complexes containing Ru–Hg and Ru–Cd bonds, for example: 432 Hz[17a] in *cis*-$Ru(CO)_3(\mu\text{-}Ph_2Ppy)(HgBr)_2$, 109.9 Hz[4b] in [*trans*-$Ru(CO)_3(\mu\text{-}Ph_2Ppy)_2HgCl]_2(Hg_2Cl_6)$ and 23 Hz[4b] in *trans*-$Ru(CO)_3(\mu\text{-}Ph_2Ppy)_2Cd(ClO_4)_2$. Our attempt to prepare a Ru–Hg complex by treating **2** with $HgCl_2$ was unsuccessful and compound **6** of formula *trans*, *cis*-$Ru(CO)_2(\mu\text{-}Ph_2PCH_2morph)_2Cl_2$ was isolated. Compound **6** was also obtained from a solution of **6** in dichloromethane or chloroform upon prolonged standing. Single crystals of the solvates **6**$\cdot CH_2Cl_2$ and **6**$\cdot 0.5CH_2Cl_2$ were obtained from crystallization of **6** from CH_2Cl_2–Et_2O and CH_2Cl_2–MeOH, respectively.

ORTEP drawings with atom numbering for molecules **4**–**6** in **4**$\cdot Et_2O$, **5**$\cdot Et_2O$, and **6**$\cdot CH_2Cl_2$ are shown in Figs. 2–4, respectively. Selected bond lengths and angles are listed in Table 2. All these complexes display a distorted octahedral geometry about the Ru atom, in which the RuP_2 unit is nearly linear with a P–Ru–P angle close to 180°. The three CO ligands and M in **4** and **5**, as well as the two CO moieties and two Cl atoms in **6**, lie in a plane perpendicular to the RuP_2 axis.

Complexes **4** and **5** are isomorphous with their iron(0) analogs.[5b] In complex **4**, the Hg atom is only three-coordinated with a Ru–Hg distance of 2.7075(4) Å, which is comparable to those of the Ru–Hg dative bond in *cis*-$Ru(CO)_3(\mu\text{-}Ph_2Ppy)(HgBr)_2$ [2.628(2) and 2.602(2) Å][17a] and *cis*-$Ru(CO)_4[HgRu_3(CO)_9(\mu\text{-}C{\equiv}C\text{-}t\text{-}Bu)]_2$ [2.658(1) and 2.655(1) Å],[17b] but shorter than those in $[Ru_6(\mu\text{-}Hg)_4(\mu\text{-}ampy)_2(CO)_{18}]$ [2.839(1), 2.859(1) and 2.841(1) Å, ampy = 2-amino-6-methyl-pyridine].[17c] The relatively long Hg(1)$\cdots$N(1) and Hg(1)$\cdots$N(2) distances of 2.790 and 3.789 Å imply that only one nitrogen atom has a weak interaction with the mercury atom (the distance of 2.790 Å is longer than the range of 2.26–2.56 Å found for mercury–tertiary amine complexes[18]).

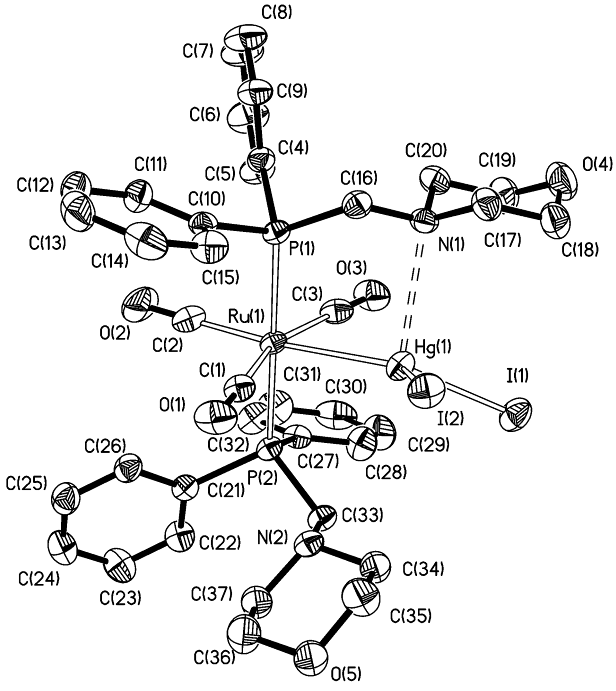


Fig. 2 Perspective view (35% thermal ellipsoids) of the molecular structure of $[Ru(CO)_3(\mu\text{-}Ph_2PCH_2morph)_2HgI_2]$ [Ph_2PCH_2morph = *N*-(diphenylphosphinomethyl)morpholine], **4**, in **4**$\cdot Et_2O$.

In complex **5**, the Cd atom is four-coordinated with a Ru–Cd bond distance of 2.7750(9) Å, which is comparable to the

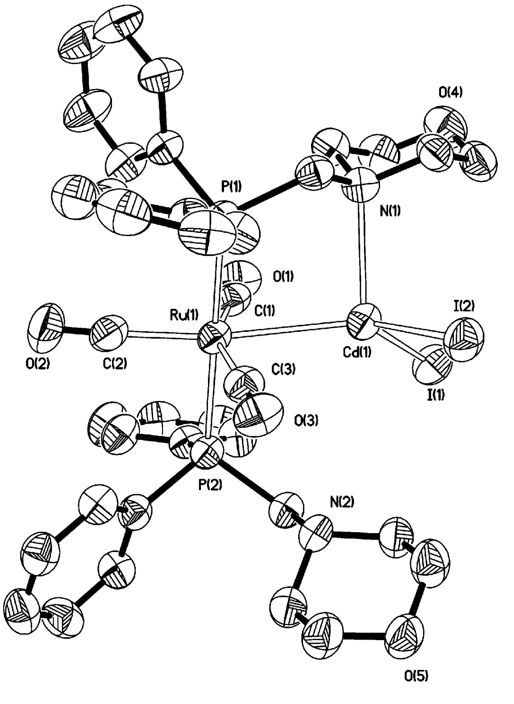


Fig. 3 Perspective view (35% thermal ellipsoids) of the molecular structure of $[Ru(CO)_3(\mu\text{-}Ph_2PCH_2morph)_2CdI_2]$, **5**, in **5**$\cdot Et_2O$.

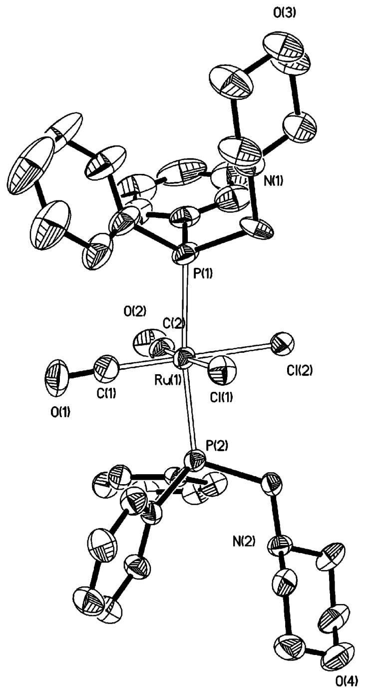


Fig. 4 Perspective view (35% thermal ellipsoids) of the molecular structure of *trans,cis*-[Ru(CO)$_2$(Ph$_2$PCH$_2$morph)$_2$Cl$_2$], **6**, in **6** · CH$_2$Cl$_2$.

sum of Ru and Cd metallic radii (2.73 Å) and those of the Ru(0)–Cd(II) dative bond in *trans*-Ru(CO)$_3$(μ-Ph$_2$Ppy)$_2$CdCl$_2$ [2.771(1) Å] and *trans*-Ru(CO)$_3$(μ-Ph$_2$Ppy)$_2$Cd(ClO$_4$)$_2$ [2.705(1) Å].[4b] This is suggestive of a strong Ru-Cd bond in compound **5**. The Cd–N distances are 2.519(5) and 4.0 Å, indicating that only one nitrogen atom is coordinated to the cadmium atom.

The 1 : 1 and 2 : 1 solvates of compound **6** with CH$_2$Cl$_2$ crystallize in different space groups: triclinic ($P\bar{1}$) and tetragonal ($I4_1/a$), respectively. Molecule **6** in **6** · CH$_2$Cl$_2$ has pseudo-C_s symmetry in which the two phosphine ligands are almost mirror images across the plane containing the Ru atom, two CO groups and two *cis* chloro ligands. In the crystal structure of **6** · 0.5CH$_2$Cl$_2$, a crystallographic C_2 axis bisects the planar Ru(CO)$_2$Cl$_2$ unit of the molecule.

Conclusion

We have successfully developed a convenient new procedure for the preparation of *trans*-Ru(CO)$_3$(L)$_2$ (L = phosphine bearing a N-donor substituent) and used the tridentate organometallic ligands **1** [L = 2-(diphenylphoshino)pyridine] and **2** [L = *N*-(diphenylphosphinomethyl)morpholine] to react with the Lewis acids AgCF$_3$SO$_3$, HgI$_2$ and CdI$_2$ to form heterobinuclear complexes containing a Ru^0 → M^{n+} [M = Ag(I), Hg(II), Cd(II)] dative bond.

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