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Diazald: An entry to diruthenium complexes containing bridging nitrosyl ligands[☆]

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Reactions of coordinatively unsaturated complexes $[Ru_2(\mu\text{-}P^tBu_2)(\mu\text{-}H)(\mu\text{-}PP)(CO)_4]$ (PP = bisphosphanes, *N*,*N*-substituted bis(diphenylphosphanyl)amines) with the nitrosylating reagent diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) were investigated. Thus a convenient synthesis affording a series of new diruthenium complexes containing bridging nitrosyl ligands of the general type $[Ru_2(\mu\text{-}P^tBu_2)(\mu\text{-}NO)(\mu\text{-}PP)(CO)_4]$ was developed and the crystal and molecular structures of five new compounds were determined. Contrary, this reaction principle does not work for the closely related complex $[Fe_2(\mu\text{-}P^tBu_2)(\mu\text{-}H)(\mu\text{-}dppm)(CO)_4]$ (dppm = $Ph_2PCH_2PPh_2$). In this case carbon monoxide was produced in side reactions and the known compound $[Fe_2(\mu\text{-}P^tBu_2)(\mu\text{-}H)(\mu\text{-}dppm)(\mu\text{-}CO)(CO)_4]$ was obtained as the main product. The molecular structure of the latter complex was also determined by X-ray diffraction.

1. Introduction

Recently we reported the synthesis and X-ray crystal structures of some new coordinatively unsaturated complexes $[Ru_2(\mu\text{-}P^tBu_2)(\mu\text{-}H)(\mu\text{-}PP)(CO)_4]$ (PP = bisphosphanes or *N*,*N*-substituted bis(diphenylphosphanyl)amines) [1]. Because of the unsaturated character of the central $Ru_2(\mu\text{-}H)$ moiety these complexes exhibit an enhanced reactivity towards a great variety of small molecules under mild conditions [2–13]. During these investigations we found that the nitrosyl ligand can be introduced conveniently in the dimetal core of $[Ru_2(\mu\text{-}P^tBu_2)(\mu\text{-}H)(\mu\text{-}dppm)(CO)_4]$ (**1**, dppm = $Ph_2PCH_2PPh_2$) by the substitution of the hydrido ligand towards NO using the nitrosylating reagent diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide). Thus the complex $[Ru_2(\mu\text{-}P^tBu_2)(\mu\text{-}NO)(\mu\text{-}dppm)(CO)_4]$ (**2**) was obtained in good yields [9]. The compound diazald was described in the literature as a useful selective nitrosylating agent especially in reactions with complexes containing hydrido ligands [14]. Now we examined this synthetic pathway for a series of other dinuclear unsaturated hydrido complexes and we describe therein the synthesis and the molecular structures of some new diruthenium complexes containing bridging nitrosyl ligands. Surprisingly this reaction principle was not successful in the case of the closely related coordinatively unsaturated diiron complex $[Fe_2(\mu\text{-}P^tBu_2)(\mu\text{-}H)(\mu\text{-}dppm)(CO)_4]$ (**3**) [15].

2. Experimental

2.1. General considerations

All preparative operations were performed under a dry nitrogen atmosphere using conventional Schlenk techniques. Solvents were dried over sodium-benzophenone ketyl or molecular sieves. The compounds **1a–f** [1,12] and **3** [15] were prepared as reported in the literature. Chemicals were purchased commercially from Aldrich. IR spectra were recorded from solid samples with a JASCO FT/IR-460 plus spectrometer equipped with an ATR unit. NMR spectra were obtained using a Jeol Eclipse 270 instrument operating at 270 (^1H) and at 109 MHz (^{31}P), respectively. Chemical shifts are given in ppm from $SiMe_4$ (^1H), and 85% H_3PO_4 (^{31}P). Microanalyses (C, H, N) were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar Vario El instrument.

2.2. Synthesis of $[Ru_2(\mu\text{-}P^tBu_2)(\mu\text{-}NO)(\mu\text{-}PP)(CO)_4]$ (PP = dmpm, **2a**; dcypm, **2b**; dppen, **2c**; dppa, **2d**; dppprа, **2e**; dppha, **2f**)

A mixture of the corresponding diruthenium complex **1a–f** (0.5 mmol) and *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (322 mg, 1.5 mmol) in diethyl ether (40 mL) was stirred for 48 h at room

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temperature. During this time the color of the solution changed from violet to green. The resulting solution was evaporated to dryness under reduced pressure. The remaining residue was dissolved in toluene and filtered over alumina using toluene as the eluent. The solvent was removed in vacuo and the products were crystallized from acetone/water (1:3) affording deep green crystals.

2a: Yield: 234 mg (75%). Anal. Calcd for $C_{17}H_{32}NO_5P_3Ru_2$ (625.51): C, 32.64; H, 5.16; N, 2.24. Found: C, 32.41; H, 5.19; N, 2.02%. IR (solid): ν(CO): 1963s, 1916vs, ν(μ-NO): 1488s. ^{1}H NMR (270 MHz, CD_2Cl_2): δ 1.80 (d, $^3J_{PH} = 14.0$ Hz, 9H, ^{t}Bu), 1.59 (m, 2H, CH_2), 1.56 (m, 6H, CH_3), 1.47 (m, 6H, CH_3), 0.88 (d, $^3J_{PH} = 14.0$ Hz, 9H, ^{t}Bu). ^{31}P{^{1}H} NMR (109 MHz, CD_2Cl_2): δ 207.7 (t, $^2J_{PP} = 130.3$ Hz, μ-P^{t}Bu$_2$), 12.1 (d, $^2J_{PP} = 130.3$ Hz, μ-dmpm). Suitable single crystals of **2a** for X-ray diffraction were obtained from water/acetone at ambient temperatures by slow evaporation during 3 days.

2b: Yield: 278 mg (62%). Anal. Calcd for $C_{37}H_{64}NO_5P_3Ru_2$ (897.98): C, 49.49; H, 7.18; N, 1.56. Found: C, 49.36; H, 7.32; N, 1.34%. IR (solid): ν(CO): 1980s, 1949vs, 1920vs, 1904vs, ν(μ-NO): 1487s. ^{1}H NMR (270 MHz, CD_2Cl_2): δ 1.84 (d, $^3J_{PH} = 13.6$ Hz, 9H, ^{t}Bu), 1.62–1.01 (m, 44H, Cy), 1.27 (m, 2H, CH_2), 0.94 (d, $^3J_{PH} = 13.5$ Hz, 9H, ^{t}Bu). ^{31}P {^{1}H} NMR (109 MHz, CD_2Cl_2): δ 216.4 (t, $^2J_{PP} = 126.8$ Hz, μ-P^{t}Bu$_2$), 55.1 (d, $^2J_{PP} = 126.8$ Hz, μ-dcypm). Suitable single crystals of **2b** for X-ray diffraction were obtained by slow diffusion of ethanol into a dichloromethane solution at room temperature within 3 days.

2c: Yield: 319 g (72%). Anal. Calcd for $C_{38}H_{40}NO_5P_3Ru_2$ (885.80): C, 51.53; H, 4.55; N, 1.58. Found: C, 51.36; H, 4.82; N, 1.24%. IR (solid): ν(CO): 1972s, 1945vs, 1933vs, 1906s, ν(μ-NO): 1490s. ^{1}H NMR (270 MHz, CD_2Cl_2): δ 7.38–7.12 (m, 20H, Ph), 6.27 (t, $^3J_{PH} = 20.5$ Hz, 2H, C=CH_2), 1.93 (d, $^3J_{PH} = 14.0$ Hz, 9H, ^{t}Bu), 1.01 (d, $^3J_{PH} = 14.0$ Hz, 9H, ^{t}Bu). ^{31}P{^{1}H} NMR (109 MHz, CD_2Cl_2): δ 211.3 (t, $^2J_{PP} = 127.9$ Hz, μ-P^{t}Bu$_2$), 41.7 (d, $^2J_{PP} = 127.9$ Hz, μ-dppen). Suitable single crystals of **2c** for X-ray diffraction were obtained from water/acetone at ambient temperatures by slow evaporation within 3 days.

2d: Yield: 284 mg (65%). Anal. Calcd for $C_{36}H_{39}N_2O_5P_3Ru_2$ (874.78): C, 49.43; H, 4.49; N, 3.20. Found: C, 49.36; H, 4.72; N, 3.44%. IR (solid): ν(CO): 2032m, 2007s, 1972vs, 1939s, ν(μ-NO): 1551vs. ^{1}H NMR (270 MHz, CD_2Cl_2): δ 7.47–7.31 (m, 20H, Ph), 1.54 (d, $^3J_{PH} = 14.2$ Hz, 9H, ^{t}Bu), 1.05 (d, $^3J_{PH} = 14.2$ Hz, 9H, ^{t}Bu). ^{31}P{^{1}H} NMR (109 MHz, CD_2Cl_2): δ 224.1 (t, $^2J_{PP} = 111.6$ Hz, μ-P^{t}Bu$_2$), 76.9 (d, $^2J_{PP} = 111.6$ Hz, μ-dppa). Suitable single crystals of **2d** for X-ray diffraction were obtained from water/acetone at ambient temperatures by slow evaporation within 3 days.

2e: Yield: 210 mg (46%). Anal. Calcd for $C_{39}H_{45}N_2O_5P_3Ru_2$ (916.86): C, 51.09; H, 4.95; N, 3.06. Found: C, 50.86; H, 4.82; N, 2.91%. IR (solid): ν(CO): 2026s, 1966s, 1944s, 1921vs, ν(μ-NO): 1615m. ^{1}H NMR (270 MHz, CD_2Cl_2): δ 7.63–7.31 (m, 20H, Ph), 3.70 (m, 2H, NCH_2), 2.55 (m, 2H, CH_2CH$_3$), 1.77 (d, $^3J_{PH} = 14.0$ Hz, 9H, ^{t}Bu), 0.88 (d, $^3J_{PH} = 14.0$ Hz, 9H, ^{t}Bu), 0.13 (m, 3H, CH$_2$CH_3). ^{31}P{^{1}H} NMR (109 MHz, CD_2Cl_2): δ 213.9 (t, $^2J_{PP} = 129.1$ Hz, μ-P^{t}Bu$_2$), 104.6 (d, $^2J_{PP} = 129.1$ Hz, μ-dpppra).

2f: Yield: 96 mg (20%). Anal. Calcd for $C_{42}H_{43}N_2O_5P_3Ru_2$ (950.88): C, 53.05; H, 4.56; N, 2.95. Found: C, 52.86; H, 4.82; N, 2.71%. IR (solid): ν(CO): 2026s, 1932s, ν(μ-NO): 1595m. ^{1}H NMR (270 MHz, CD_2Cl_2): δ 7.85–6.79 (m, 25H, Ph), 1.37 (d, $^3J_{PH} = 14.5$ Hz, 9H, ^{t}Bu), 1.08 (d, $^3J_{PH} = 13.2$ Hz, 9H, ^{t}Bu). ^{31}P{^{1}H} NMR (109 MHz, CD_2Cl_2): δ 221.1 (t, $^2J_{PP} = 133.8$ Hz, μ-P^{t}Bu$_2$), 104.7 (d, $^2J_{PP} = 133.8$ Hz, μ-dppha). Suitable single crystals of **2f** for X-ray diffraction were obtained from water/acetone at ambient temperatures by slow evaporation within 3 days.

2.3. *Reaction of [Fe_2(μ-P^{t}Bu$_2$)(μ-H)(μ-dppm)(CO)$_4$](**3**) with diazald*

Compound **3** (377 mg, 0.5 mmol) was dissolved in diethyl ether (30 mL), diazald (322 mg, 1.5 mmol) was added and the resulting solution stirred at room temperature. After 5 h the deep green color of the solution was changed to red–brown. The solution was stirred for additional 15 h and the solvent was removed under reduced pressure. (During this procedure, the liquid in the vacuum trap adopted an orange color. In the liquid the presence of the volatile [$Fe(CO)_2(NO)_2$] was indicated by IR spectroscopy.) The remaining residue was extracted three times with 10 mL portions of diethyl ether. The combined extracts were filtered over a short column of alumina with diethyl ether as the eluent affording an orange–brown band. The investigation of this fraction by ^{31}P NMR spectroscopy showed unambiguously the presence of complex **5** (traces) and **4**, respectively [18,15]. Finally, compound **4** was obtained by crystallization from CH_2Cl_2/ethanol as orange–brown crystals suitable for X-ray diffraction. Yield: 172 mg (44%). Anal. Calcd for $C_{38}H_{41}Fe_2O_5P_3$ (782.36): C, 58.34; H, 5.28. Found: C, 58.12; H, 5.33%. ^{31}P{^{1}H} NMR (109 MHz, CD_2Cl_2): δ 240.0 (t, $^2J_{PP} = 42.8$ Hz, μ-P^{t}Bu$_2$), 74.2 (d, $^2J_{PP} = 42.8$ Hz, μ-dppm). The ^{1}H NMR and IR data were reported elsewhere [15].

2.4. *X-ray structural determination*

Suitable single crystals for X-ray diffraction of the compounds **2a**–**d** and **2f** were obtained as described in the experimental section. Crystals were selected by means of a polarization microscope, mounted on the tip of a glass fiber, and investigated on a Bruker Nonius-Kappa CCD diffractometer (**2a**–**c**, **2f**, and **4**) and on an Oxford XCalibur diffractometer (**2d**), respectively, using Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS) [16] and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) [17]. The position of the hydrido ligand in compound **4** has been located from the difference map. Details of the crystal data, data collection, structure solution, and refinement parameters of the new compounds are summarized in Table 1 (**2a**–**c**) and Table 2 (**2d**, **2f**, and **4**), respectively.

Table 1
Crystal data and structure refinement details for compounds **2a**–**c**.

Compound	**2a**	**2b**	**2c**·1.5 acetone
Empirical formula	$C_{17}H_{32}NO_5P_3Ru_2$	$C_{37}H_{64}NO_5P_3Ru_2$	$C_{42.5}H_{49}NO_{6.5}P_3Ru_2$
Formula weight	625.9	897.94	972.88
Temperature (K)	173(2)	173(2)	173(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pnma*	$P2_1/c$	$P2_1/c$
a (Å)	14.9069(6)	18.1026(2)	16.6252(2)
b (Å)	14.9333(6)	18.2483(2)	13.6152(2)
c (Å)	11.1729(5)	12.78950(10)	18.7877(3)
α (°)	90	90	90
β (°)	90	104.1180(10)	93.2720(10)
γ (°)	90	90	90
Volume (Å^3)	2487.19(18)	4097.29(7)	4245.77(11)
Z	4	4	4
ρ_{calcd} (g cm^{-3})	1.670	1.456	1.522
μ/mm^{-1}	1.433	0.894	0.872
θ range for data collection (°)	3.29–27.48	3.21–27.56	3.18–27.49
Reflections measured	16,607	35,193	32,845
R_{int}	0.1243	0.0343	0.0332
Observed reflections	2948	9423	9723
Reflections, unique	9076	18,382	17,748
Parameters/ restraints	156/0	453/0	524/0
R (F_{obs})	0.0421	0.0312	0.0279
R_w (F^2)	0.0956	0.0777	0.0605
S	1.060	1.039	1.067
Max electron density (e Å^{-3})	0.830	0.555	0.642
Min electron density (e Å^{-3})	−0.606	−0.516	−0.605